A Study of Processing of Indium Doped Semiconductor Material.

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CONTENTS

ABSTRACT

Indium- doped Silicon is being investigated as an extrinsic photoconductor material for use in the 3 to 5 μm infrared region. The low indium concentration obtained by standard growth methods and presence of a shallower defect level associated with the indium. The concentration of indium in float zone grown crystals is generally even lower than this because of the low segregation co-efficient of indium.

A shallower defect Centre associated with indium and labelled as indium. It is observed that in Hall co-efficient measurements at energy of about 0.11eV.

Solution growth techniques such as gradient –transport solution growth and LPE have been used to grow III – V compound. The use of temperature – gradient zone melting as a means of producing large area p – n junctions in silicon. An important feature of this solution growth procedure is that the crystals are grown the melting point of silicon.so the retrograde solubility of the impurities can be used to obtain very heavily doped crystals.

In the present work Indium is doped on silicon metal inside a micro-oven at the temperature of 200^0C.Different samples are kept inside the micro-oven for different time period. After that XRD,SEM and V-I characteristics have been done, then voltage drop is calculated and different peaks have come and changes in micro structure have been found.

INTRODUCTION

The modern concept of electrical resistance was first discovered by G. S. Ohm, in 1926, who formulated the famous equation: V=IR, while working on direct-current circuit. The resistance is a function of temperature and stress for a given material. This property of resistance is employed in resistance-temperature conversion.

1.1 RESISTANCE AND ITS ORIGIN:

The electrical resistance of an object is a measure of its opposition to the passage of an electric current. Electrical resistance of a circuit component or device is defined as the ratio of the voltage applied to the electric current which flows through it.

I V R □

The SI unit of electrical resistance is the ohm (Ω). Resistance's reciprocal quantity is electrical conductance measured in siemens.

1.1.1 Causes of resistance:

In metals:

When an electrical potential difference (a voltage) is applied across the metal, the electrons drift from one end of the conductor to the other, under the influence of the electric field. Near room temperatures, the thermal motion of ions is the primary source of scattering of electrons (due to destructive interference of free electron waves on non-correlating potentials of ions), and is thus the prime cause of metal resistance. Imperfections of lattice also contribute into resistance, 10 although their contribution in pure metals is negligible. The longer the conductor, the more scattering events occur in each electron's path through the material, so the higher the resistance [1].

In semiconductor and insulator:

In semiconductors the position of the Fermi level is within the band gap, approximately half-way between the conduction band minimum and valence band maximum for intrinsic (undoped) semiconductors. This means that at zero kelvin, there are no free conduction electrons and the resistance is infinite. However, the resistance will continue to decrease as the charge carrier density

in the conduction band increases. In extrinsic (doped) semiconductors, dopant atoms increase the majority charge carrier concentration by donating electrons to the conduction band or accepting holes in the valence band. For both types of donor or acceptor atoms, increasing the dopant density leads to a reduction in the resistance. Highly doped semiconductors hence behave like metallic. At very high temperatures, the contribution of thermally generated carriers will dominate over the contribution from dopant atoms and the resistance will decrease exponentially with temperature [1].

1.1.2 Temperature dependence of resistance:

Near room temperature, the electrical resistance of a typical metal increases linearly with increase in temperature, while the electrical resistance of a typical semiconductor decreases with rising temperature. To the first order, the temperature dependence of resistance follows the relation

where, T is its temperature, $T0$ is a reference temperature (usually zero Kelvin or room temperature), R_0 is the resistance at $T0$, and α is the coefficient of change in resistivity per unit temperature also known as, temperature coefficient of resistance. The constant α depends only on the material being considered.

Intrinsic semiconductors become better conductors as the temperature increases; the electrons are jumped to the conduction energy band by thermal energy, where they flow freely and in doing so leave behind holes in the valence band which also flow freely. The electric resistance of a typical intrinsic (non-doped) semiconductor decreases exponentially with rise temperature:

Extrinsic (doped) semiconductors have a far more complicated temperature profile. As temperature increases starting from absolute zero, they first decrease steeply in resistance as the carriers leave the donors or acceptors. At higher temperatures it will behave like intrinsic semiconductors as the carriers from the donors/acceptors become insignificant compared to the thermally generated carriers[1].

1.2 RESISTIVITY

The quantitative measure of a material‟s opposition to the flow of current is called resistivity. It depends only on the composition of the material and not on the shape and size.

where: R is the resistance(ohms), ρ is resistivity(ohm-meters), L is the length(meters), and A is the cross-sectional area(square-meters).

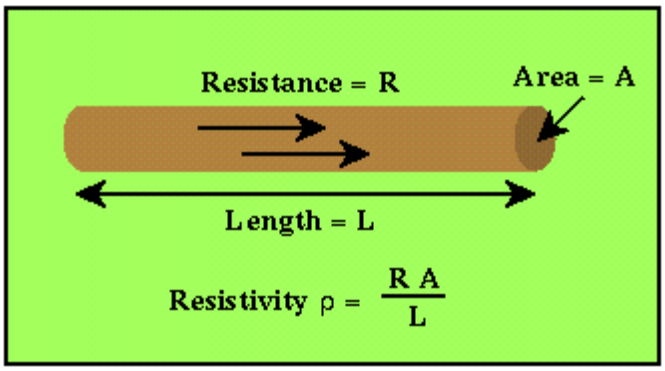


Fig 1.1: Resistivity of a material [3]

Although the resistivity is temperature dependent, it can be used to calculate the resistance of a wire of given geometry at a given temperature.

The resistivity of the material changes with temperature. For many materials, the change is a simple linear function of temperature: , where: ρ(T) = resistivity at temperature T, ρ_0 =resistivity at temperature T0, α =temperature coefficient of resistivity [4].

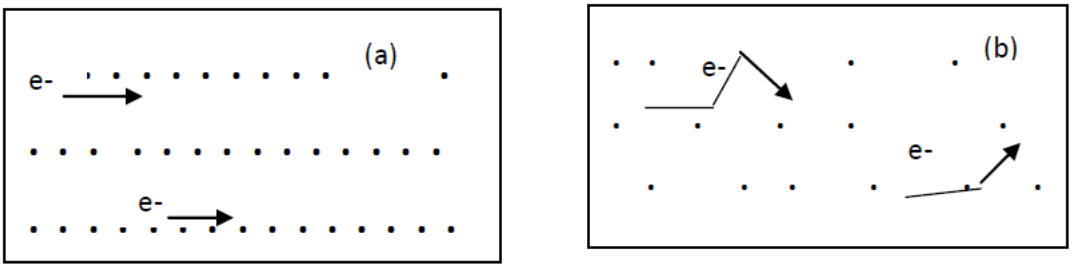


Fig 1.2: movement of electron in (a) cold body (b) hot body. In cold body, the ions are more ordered and the electrons move without much scattering. In hot body, due to vibration of ions, the electrons undergo more scattering.

Materials	Resistivity, ρ(ohm-meter)
Metals	10−8
Semiconductors	Variable
Electrolytes	Variable

Insulators	1016
Superconductors	0(exactly)

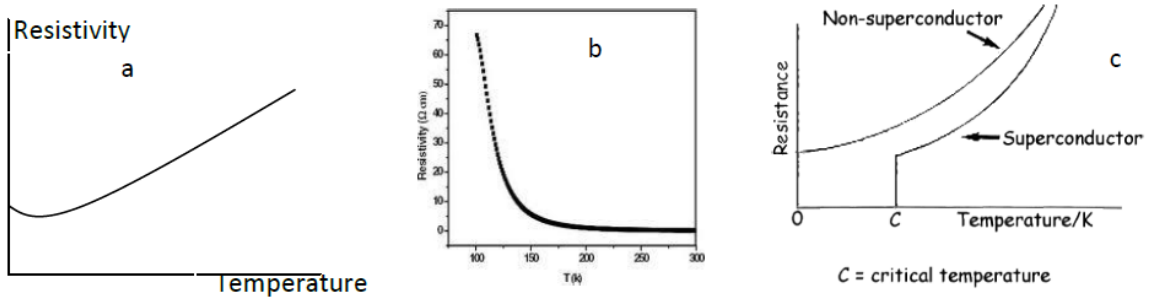


Fig 1.3: Resistivity vs. temperature plot for a) metal b) semiconductor c) superconductor

Table 1.1 shows the resistivity of the various materials. The temperature dependent of resistivity of the various materials as shown in Figure 1.3.

1.3 MATERIALS DESCRIPTION

Silicon, a tetravalent metalloid, is a chemical element with the symbol **Si** and atomic number 14. It is less reactive than its chemical analog carbon, the nonmetal directly above it in the periodic table, but more reactive than germanium, the metalloid directly below it in the table. It was first prepared and characterized in pure form in 1823. In 1808, it was given the name silicium (from Latin: *silicis*, flints), with an **-ium** word-ending to suggest a metal, a name which the element retains in several non-English languages. However, its final English name, first suggested in 1817, reflects the more physically similar elements carbon and boron.

Silicon is the eighth most common element in the universe by mass, but very rarely occurs as the pure free element in nature. It is most widely distributed in dusts, sands, planetoids, and planets as various forms of silicon dioxide (silica) or silicates. Over 90% of the Earth's crust is composed of silicate minerals, making silicon the second most abundant element in the Earth's crust (about 28% by mass) after oxygen.

Most silicon is used commercially without being separated, and indeed often with little processing of compounds from nature. These include direct industrial building-use of clays, silica sand and stone. Silica is used in ceramic brick. Silicate goes into Portland cement for mortar and stucco, and when combined with silica sand and gravel, to make concrete.

Silicates are also in whiteware ceramics such as porcelain, and in traditional quartz-based soda-lime glass. More modern silicon compounds such as silicon carbide form abrasives and high-strength ceramics. Silicon is the basis of the ubiquitous synthetic silicon-based polymers called silicones.

Elemental silicon also has a large impact on the modern world economy. Although most free silicon is used in the steel refining, aluminum-casting, and fine chemical industries (often to make fumed silica), the relatively small portion of very highly purified silicon that is used in semiconductor electronics (< 10%) is perhaps even more critical. Because of wide use of silicon in integrated circuits, the basis of most computers, a great deal of modern technology depends on it.

Silicon is an essential element in biology, although only tiny traces of it appear to be required by animals. However, various sea sponges as well as microorganisms like diatoms need silicon in order to have structure. It is much more important to the metabolism of plants, particularly many grasses.

Indium is a chemical element with symbol **In** and atomic number 49. This rare, very soft, malleable and easily fusible post-transition metal is chemically similar to gallium and thallium, and shows intermediate properties between these two. Indium was discovered in 1863 and named for the indigo blue line in its spectrum that was the first indication of its existence in zinc ores, as a new and unknown element. The metal was first isolated in the following year. Zinc ores continue to be the primary source of indium, where it is found in compound form. Very rarely the element can be found as grains of native (free) metal, but these are not of commercial importance.

Indium's current primary application is to form transparent electrodes from indium tin oxide (ITO) in liquid crystal displays and touchscreens, and this use largely determines its global mining production. It is widely used in thin-films to form lubricated layers (during World War II it was widely used to coat bearings in high-performance aircraft). It is also used for making particularly low melting point alloys, and is a component in some lead-free solders.

Indium is not known to be used by any organism. In a similar way to aluminium salts, indium(III) ions can be toxic to the kidney when given by injection, but oral indium compounds

do not have the chronic toxicity of salts of heavy metals, probably due to poor absorption in basic conditions. Radioactive indium-111 (in very small amounts on a chemical basis) is used in nuclear medicine tests, as a radiotracer to follow the movement of labeled proteins and white blood cells in the body.

1.4 OBJECTIVE:

The objectives of the research are :

- To design a indium dopped silicon semiconductor.
- To prepare a sample for voltage drop study.
- To study the current dependent of the sample prepared.

Indium doped silicon has been grown from indium – rich solutions using a gradient – transport solution growth process. The growth temperatures were varied from 150^0c to 200^0c inside a micro-oven to determine the voltage drop of indium in silicon. The indium concentration obtainedin silicon. The growth process is described by one-dimensional diffusion .The solution –grown crystals were found to have a lower concentration of this shallower defect than melt grown crystals of the same indium concentration. The Oxygen and carbon concentrations are less because the sample is heated inside the microoven.

2.1 literature Review

2.1.1 NANOPARTICLES

Nanomaterials are applications with morphological features smaller than a one tenth of a micrometre in at least one dimension. Despite the fact that there is no consensus upon the minimum or maximum size of nanomaterials, with some authors restricting their size to as low as 1 to ~30 nm, a logical definition would situate the nanoscale between microscale (0.1 micrometre) and atomic/molecular scale (about 0.2 nanometers). An aspect of nanotechnology is the vastly increased ratio of surface area (second power of its linear dimensions) to volume (third power of its linear dimensions) present in many nanoscale materials which makes possible new quantum mechanical effects, for example the "quantum size effect" where the electronic properties of solids are altered with great reductions in particle size. This effect does not come into play by going from macro to micro dimensions. However, it becomes pronounced when the nanometer size range is reached. A certain number of physical properties also alter with the change from macroscopic systems. Novel mechanical properties of nanomaterials is a subject of nanomechanics research. Catalytic activities also reveal new behaviour in the interaction with biomaterials.

Nanotechnology can be thought of as extensions of traditional disciplines towards the explicit consideration of these properties. Additionally, traditional disciplines can be re-interpreted as specific applications of nanotechnology. This dynamic reciprocation of ideas and concepts contributes to the modern understanding of the field. Broadly speaking, nanotechnology is the synthesis and application of ideas from science and engineering towards the understanding

and production of novel materials and devices. These products generally make copious use of physical properties associated with small scales.

Electronic states of an atom are typically characterized by discrete energy levels that are often separated by electron volts. The spatial distribution of these states is highly localized. At the nanoscale, the dimension of energy states resides between these limits. Considering an electron of mass '*m*' confined within a one-dimension (1-D) box of size '*L*' and moving along x-axis inside the box, where potential energy $V(x) = 0$, the time-independent Schrodinger wave equation is given as [8]:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \tag{2.1}$$

Where E is the total energy of the particle, or

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \tag{2.2}$$

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \tag{2.3}$$

Where, $k = \sqrt{\frac{2mE}{\hbar^2}}$ (2.4)

For a particular value of the energy E, k is a constant.

The general solution of the above Eq. (2.3) is

$$\psi(x) = A\sin kx + B\cos kx \tag{2.5}$$

Where A and B are constant of integration. We have the boundary conditions: (a) at x =0, $\psi(x) = 0$ and (b) at $x = L$, $\psi(x) = 0$.

From the first condition, we get $B = 0$. Therefore, from Eq. (2.5) we have

$$\psi(x) = A \sin kx \tag{2.6}$$

Again, from the second boundary condition, we have

$$\psi(L) = A \sin kL = 0 \tag{2.7}$$

We cannot take A=0, because there will be no solution. Hence Eq. (2.7) is satisfied only when, $kL = n\pi$ (where n = 1, 2, 3….), or

$$kL = n\pi \tag{2.8}$$

We cannot take n = 0, because for n = 0, k = 0, E = 0 and hence $\psi(x) = 0$ everywhere in the box. This means that a particle with zero energy cannot present in the box. That is, a particle in a box, cannot have zero energy. Substituting the value of k from (2.8) in Eq. (2.4), we have

$$\sqrt{\frac{2mE}{\hbar^2}} = \frac{n\pi}{L} \tag{2.9}$$

From the above equation we get

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2} \tag{2.10}$$

This equation represents the eigen-values of the energy and is also called energy-levels of the particle. Since, $\hbar = \frac{h}{2\pi}$, we can have

$$E = \frac{n^2 h^2}{8mL^2} \tag{2.11}$$

The lowest energy level of this system is given by $E = (h^2 / 8\, m\, L^2)$, where 'h' is the Planck's constant and 'm' is the mass of the particle (electron). Since, $E \propto 1/L^2$, if size of the box (particle diameter) is reduced, then E increases, hence a drastic variation of its bulk properties. In the nanoscale phenomena, the energy level spacing of electronic states of atom increases with reduction in dimensionality of particle and is called Quantum Confinement (QC) [9], and is shown in Fig. 2.1. On the other word QC describes the increase in energy which occurs when the motion of a particle is restricted in one or more dimensions by a potential well. When the confining dimension is large compared to the wavelength of the particle, the particle behaves as if it were free. As the confining dimension decreased, the particle's energy increases.

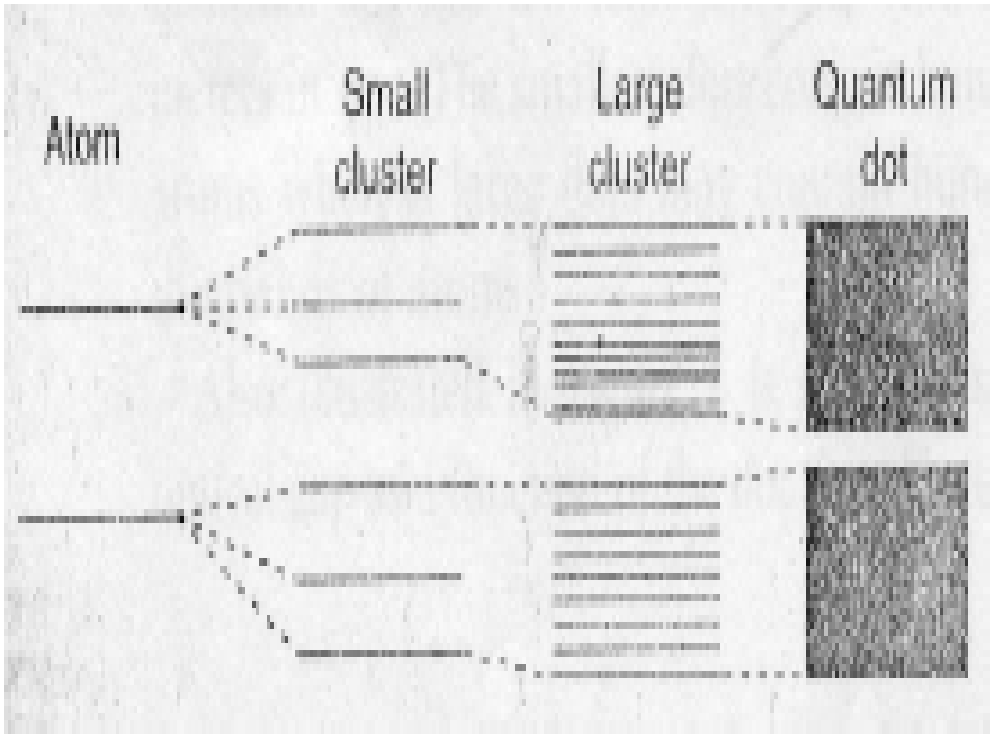


Fig. 2.1 Energy level diagram (atom, cluster and quantum dot)

The QC phenomena can be readily understood from the well known Heisenberg Uncertainty principle, which states that:

$$\Delta P.\Delta x = \hbar / 2 ,$$

$$\Delta P = \hbar / 2.\Delta x .$$

Where Δp- uncertainty in momentum, and Δx- uncertainty in position

A free electron confined within a 1-dimension box of size "*L*" (i.e. Δx)

$$\Rightarrow E \propto 1/(L)^2$$

Hence, if one tries to localize the position of an electron by reducing the box size (*L*), its energy must increases and diverge as the confining region vanishes.

Considering the energy of a free electron with momentum *P*, i.e.,

$$E = P^2 / 2m$$

Since the uncertainty in momentum cannot exceed the momentum itself *P*, i.e., $P > \Delta P$. So, the energy can be defined as $E < \hbar^2 / 8m L^2$. If one tries to localize the position of an electron by reducing the box size (*L*), its energy must increases and diverges as the confining region vanishes. QC can be experimentally observed in nanostructures quantum dots of Si and CdSe. Typically a quantum dot is a few nanometers to tens of nanometer size. The smallest dots contain hundreds of thousands of atoms. However, nanocrystalline materials are single-phase or multi-phase polycrystals, the crystal size of the order of 1-100 nm in at least 1-D. Depending on the QC and dimensions in which the length scale is nanometers, they can be classified [10] into:

(a) nanoparticles (0-D), (b) lamellar structure (1-D), (c) filamentary structure (2-D), and (d) bulk nanostructured (3-D) materials.

2.1.2 FERROELECTRICITY

Ferroelectricity is a spontaneous electric polarization of a material that can be reversed by the application of an external electric field. [11, 12]. The term is used in analogy to ferromagnetism, in which a material exhibits a permanent magnetic moment. Ferromagnetism was already known when ferroelectricity was discovered in 1920 in Rochelle salt by Valasek [13, 14]. Thus, the prefix *ferro*, meaning iron, was used to describe the property despite the fact that most ferroelectric materials do not have iron in their lattice.

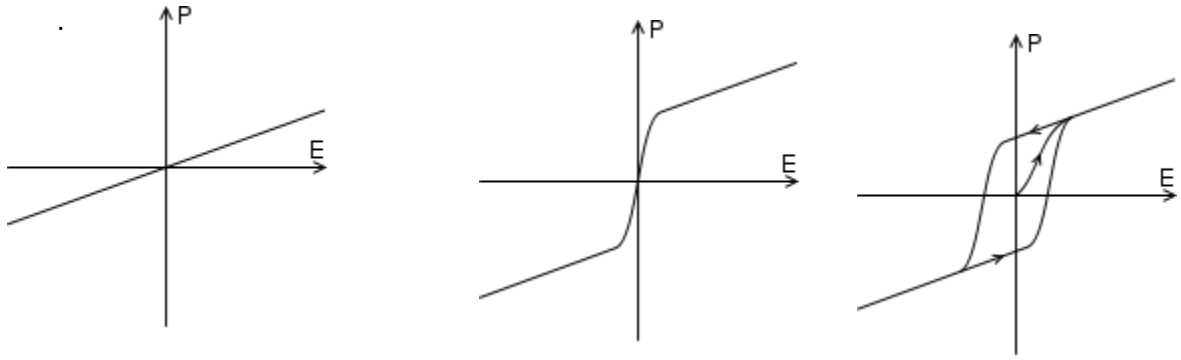


Fig. 2.2 Polarization: (a) Dielectric (b) Paraelectric (c) Ferroelectric

Most materials are polarized linearly with external electric field; nonlinearities are insignificant. This is called dielectric polarization, Fig. 2.2 (a). Some materials, known as paraelectric materials, demonstrate a more pronounced nonlinear polarization, Fig. 2.2 (b). The

electric permittivity, corresponding to the slope of the polarization curve, is thereby a function of the external electric field. In addition to being nonlinear, ferroelectric materials demonstrate a spontaneous polarization, Fig. 2.2 (c). Such materials are generally called pyroelectrics. The distinguishing feature of ferroelectrics is that the direction of the spontaneous polarization can be reversed by an applied electric field, yielding a hysteresis loop. Typically, materials demonstrate ferroelectricity only below a certain phase transition temperature, called the Curie temperature, T_c, and are paraelectric above this temperature.

2.1.3 PHYSICS OF FERROELECTRICITY

When the field F is reduced to zero a finite value of polarization called remanent polarisation P_r can be measured. In order to eliminate the remanent polarization P_r, an electric field of opposite direction must be applied. This is called the coercive force F_c. If the linear part of the hysteresis loop occurring at sufficiently large applied field strengths is extrapolated back to the polarization axis, one obtains the value of the spontaneous polarization P_S.

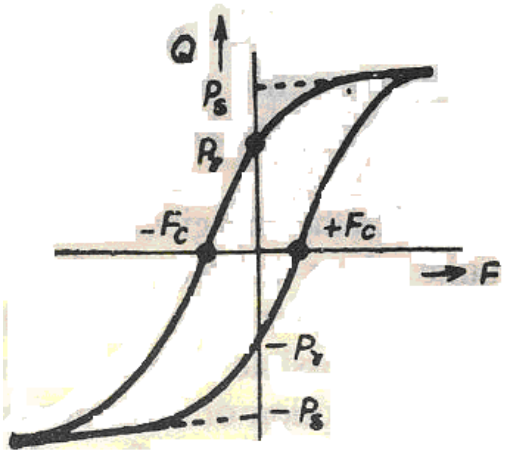


Fig. 2.3 Hysteresis Loop

The occurrence of hysteresis loop is understandable on the basis of the domain structure. In unpolarized materials a domain has equal chance of being polarized positively and negatively. If a field is applied, new positively polarized domains will grow at the expense of negatively polarized domains; the number of new domains increases at first slowly, then more rapidly, until finally all domains are lined up in the direction of the applied field. If the applied field is now reduced to zero many domains will remain aligned thus causing a permanent polarization P_r. An opposing electric field $-F_C$ has to be applied in opposite direction to remove this alignment. If the opposing field is large the material will gradually become polarized in opposite direction until saturation polarization sets in. If the field is now reduced to zero many domains remain aligned thus causing the remanent polarization $-P_r$; an opposing field $+F_C$ has to be applied to remove this alignment.

Energy is lost if the polarization is run through a complete cycle; the loss of energy per unit volume per cycle is $\oint E$ dP. This is important for a –c operation; if a sufficiently large signal of frequency *f* is applied, the power loss P_{hyst} of the sample is

$$P_{hyst} = \int V_S \oint F.dP$$

where *F* is the electric field and *V* is the volume of the sample.

A single crystal material is very suitable for the determination of the saturation polarization P_S. It is rather impossible to line up all the domains in the directions of the applied field since in general the directions of preferred polarization of a crystallite do not coincide with the applied field; a polycrystalline material is not very suitable for a determination of P_S.

2.1.4 FERROELECTRICS

The internal electric dipoles of a ferroelectric material are coupled to the material lattice so anything that changes the lattice will change the strength of the dipoles (in other words, a change in the spontaneous polarization). The change in the spontaneous polarization results in a change in the surface charge. This can cause current flow in the case of a ferroelectric capacitor even without the presence of an external voltage across the capacitor. Two stimuli that will change the lattice dimensions of a material are force and temperature. The generation of a surface charge in response to the application of an external stress to a material is called piezoelectricity. A change in the spontaneous polarization of a material in response to a change in temperature is called pyroelectricity.

Ferroelectric phase transitions are often characterized as either displacive (such as $BaTiO_3$) and order-disorder (such as $NaNO_2$), though often phase transitions will have behavior that contains elements of both behaviors. In barium titanate, a typical ferroelectric of the displacive type, the transition can be understood in terms of a polarization catastrophe, in which, if an ion is displaced from equilibrium slightly, the force from the local electric fields due to the ions in the crystal increases faster than the elastic-restoring forces. This leads to an asymmetrical shift in the equilibrium ion positions and hence to a permanent dipole moment. The ionic displacement in barium titanate concerns the relative position of the titanium ion within the oxygen octahedral cage.

2.1.5 CHARACTERISTICS

Of the 32 possible crystal classes (i.e. point groups) 11 are Centro symmetric and thus cannot exhibit polar properties. The remaining 21 lack a center of symmetry and thus can posses one or more polar axes. Of these, 20 classes are piezoelectric (the one exception being cubic class 432). Piezoelectric crystals have the property that the application of mechanical stress induces polarization, and conversely, the application of an electric field produces mechanical deformation. Of the 20 piezoelectric classes, 10 have a unique polar axis and thus are spontaneously polarized, i.e. polarized in the absence of an electric field. Crystals belonging to polarized, i.e. polarized in the absence of an electric field. Crystals belonging to these 10 classes are called pyroelectric. The intrinsic polarization of pyroelectric crystals is often difficult to detect experimentally because of the neutralization of the charges on the crystal surfaces by free charges from the atmosphere and by conduction within the crystal. However, because the polarization is a function of temperature, it is often possible to observe the spontaneous moment in these crystals by changing the temperature, hence the name pyroelectrics. Ferroelectric crystals belong to the pyroelectric family, but they also exhibit the additional property that the direction of the spontaneous polarization can be reversed by the application of an electric field. Thus, we have the following simple definition for a ferroelectric crystal: **A ferroelectric crystals is a crystal that possess reversible spontaneous polarization as exhibited by a dielectric hysteresis loop.**

Although ferroelectric crystals are a widely varied group, they posses a number a general characteristics properties. Among these are the following:

- Which the crystal behaves as a normal dielectric. It should be noted, however, that in some crystals melting or chemical decomposition may occur before the Curie point is reached (e.g., the FE polymer PVDF).

- The hysteresis loop disappears at a certain temperature, the Curie point T_c, above at T_c a ferroelectric crystal transforms to a phase of higher symmetry. This higher temperature phase is usually nonpolar, or Para electric (PE).
- The polar crystal structure of a ferroelectric can be derived from the high-temperature PE structure by a slight distortion of the crystal lattice. This is the main reason behind the success of the phenomenological theory of Ferro electricity which assumes that the same free energy function is applicable for both the FE and PE phases.
- Ferroelectrics generally have a large static dielectric constant ε , or χ (= *P/E*, is the susceptibility), which rises to a peak value at T_c.
- Above T_c, ε of a ferroelectric (measured along the polar axis) usually obeys the Curie-Weiss law $\varepsilon = C/(T-T_0)$, where C and T_0 are the Curie-Weiss constant and Curie-Weiss temperature, respectively.

Finally, we should mention that there are substances which, on cooling, undergo a transition from a nonpolar to an anti polar state. In this state the crystal has a super lattice consisting a arrays of antiparallel dipoles. If, in a given crystal, the coupling energy between these arrays is comparable to that of the polar case, then the crystal is said to be anti ferroelectric (AFE). An anti ferroelectric crystal can usually be made ferroelectric by the application of a sufficiently large electric field.

2.1.6 THEORY OF FERROELECTRICITY

A shift of ionic positions as for Ti ion in $BaTiO_3$ is the key to Ferro electricity. Imagine a crystal just before it goes into ferroelectric phase. Suppose that an infinitesimal displacement of an ion from its equilibrium position occurs, then a local electric field is created on account of the dipole moment associated with the displacement. If the electric force overcomes the elastic restoring force a further displacement of the ion is expected. As displacement becomes appreciable anharmonic restoring forces set in and the ion finds itself in a new equilibrium position corresponding to the position which the ion occupies in the ferroelectric phase.

To explain the electric behavior of a specific ferroelectric crystal, a detailed knowledge of the particular arrangement of electric charges and forces in a given crystal structure is needed and then a specific model can be set up for the crystal under consideration [15]. Such model theories are available for Barium Titanate, Rochelle salt and potassium di hydrogen phosphate.

From the force balance we can write the following equation

$$A\,E_{loc} = Bx + Cx^3 + Dx^5$$

where E_{loc} is the local field acting on and x is the displacement of the ion under consideration and the constants A, B, C and D are proportionality constants. The terms involving x^3 and x^5 represent the anharmonic components of the restoring force. Since the dipole moment and in turn the polarisation P created by the displacement are directly proportional to x. Eq. (3.2) can be expressed in terms of P as

$$E_{loc} = aP + bP^3 + cP^5$$

The local field can also be written as

$$E_{loc} = E + f\,P$$

where E is the applied field and a general polarisation field $f P$ is used instead of the Lorentz field $P/3 \in_0$. Eqs. (3.4) with equation (3.3) gives

$$E = (a - f) P + bP^3 + cP^5$$

Therefore the internal energy of the system is equal to

$$U = \int EdP = \frac{(a-f)P^2}{2} + \frac{bP^4}{4} + \frac{cP^6}{6}$$

Two cases of particular interest in ferroelectric phase.

Case 1. (a - f) and c are positive while b is negative. In this case the spontaneous polarisation jumps discontinuously from zero to a finite value at the Curie temperature T_c. The zero value corresponds to the dielectric phase and the non-zero value to the ferroelectric phase. Since these two states exist simultaneously at T_c.

$$\frac{(a-f)P_s^2}{2} + \frac{bP_s^4}{4} + \frac{cP_s^6}{6} = U_p = U_0 = 0$$

where P_s is the spontaneous polarisation and the subscripts p and o refer to the polarised and unpolarized state respectively. Furthermore P_s exists in the absence of E, thus from we have

$$(a - f) + bP_s^2 + cP_s^4 = 0$$

Eqs. give the following results:

$$P_s^2(T_c) = -\frac{3b}{4c} = -\frac{4(a-f)}{b}$$

$$P_s^4(T_c) = \frac{3(a-f)}{c}$$

Case 2. $(f - a)$ and b are positive while c is negligible. It is obvious that with c = 0, the only solution of is

$$P_c^2(T_c) = 0 \text{ and } (f - a) = 0 \text{ at T = } T_c$$

Now let us look up the dielectric phase. Differentiating we get

$$\in - \in_0 = \frac{\partial P}{\partial E} = \frac{1}{a - f}$$

noting that the terms involving P_3 and P_5 are negligibly small compared to the linear term in P on account of the smallness of P in the dielectric phase.

For case (2) we can expand $(a - f)$ into a power series in terms of T-T_c. If only the first order term is kept, $\in - \in_0$ must be of the following form

$$\in - \in_0 = \frac{\beta}{T - T_c}$$

since $a - f = 0$ at T=T_c

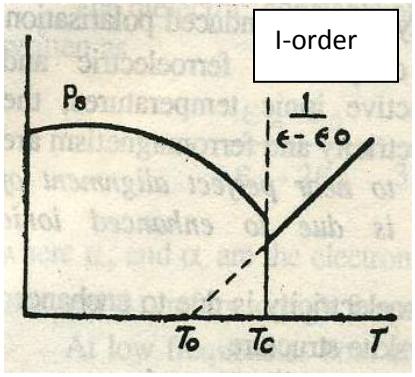
For case (1) $(a - f)$ is not zero at T=T_c. Therefore expansion at another *temperature* T_0 where $a - f$ is necessary. Thus for case (1) we have

$$\in - \in_0 = \frac{\beta}{T - T_0}$$

Behaviour of P_s and $\in$ as a function of temperature is illustrated in Fig. 2.4.

Case (1) and case (2) are known thermodynamically as first order and second order transitions respectively since case (1) involves a latent heat of transition while case II do not.

Barium Titanate shows the characteristics of a first order transition, potassium dihydrogen phosphate and Rochelle salt show the characteristics of a second order transition.



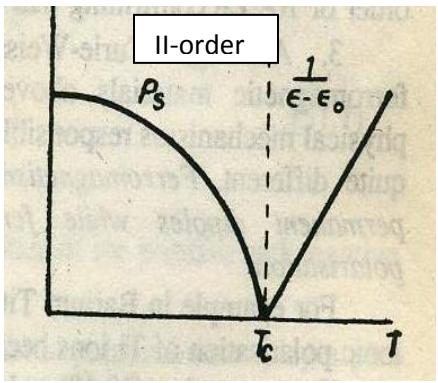


Fig. 2.4 The P_s and $\in$ as a function of temperature

Points of Interest

1. If ferroelectricity was due to an alignment of permanent dipoles the value of f should be different from *1/3* $\in_0$ even for crystals with cubic symmetry i.e. Lorentz's approach for internal field becomes inapplicable. Since Lorentz's approach is valid, the polarisation is included by a strain-inspired field.
2. If ferroelectricity was due to dipole alignment the value of β predicted is $\beta=3T_0\in_0$, while experimentally measured value of β is of the order of 10^5 $\in_0$ confirming that ferro electricity is due to induced polarization.
3. Although Curie-Weiss Law is obeyed in ferroelectric and ferromagnetic materials above their respective ionic temperatures, the physical mechanisms responsible for Ferro electricity and ferromagnetism are quite different. Ferromagnetism arises due to near perfect alignment of permanent dipoles while Ferro electricity is due to enhanced ionic polarization.

For example in Barium Titanate the Ferro electricity is due to enhanced ionic polarization of Ti ions because of Perovskite structure.

From Eq. (3.11) polarization catastrophe will occur when

$$\frac{\partial P}{\partial E} = \infty, i.e. (a - f) = 0$$

Since $a = \frac{1}{N\alpha}$ and $f = \frac{1}{3\in_0}$

Therefore polarisation catastrophe is expected when $\frac{N\alpha}{3\in_0} = 1$

The electronic contribution to the polarisability α can be estimated from the optical refractive index n of Ba TiO_3

$$\frac{n^2-1}{n^2+2}=\frac{N\alpha_e}{3\in_0}$$

For a value of n = 24, the value of $\frac{N\alpha_e}{3\in_0}$ is found to be 0.61. This leaves of value of 0.9 for ionic polarisation.

In Barium Titanate the Ti (ions) by their polarisation polarise the oxygen (type O_1) ions and these in turn act back on the Ti ions resulting in linear chains of dipoles. Since the oxygen (type O_1) ions in this linear chain do not possess cubic symmetry the field factor f is very much larger than $1/3\in_0$. It is thus great enhancement of the field at the Ti ion which causes the polarization of the Ti ion and makes the value of $fN\alpha_i(Ti)$ large enough for the polarization catastrophe.

Since the fundamental mechanics responsible for spontaneous polarization in many materials is not identifiable except for Barium Titanate which is most extensively investigated and best understood.

There are difficulties in formulating a unified theory of ferroelectricity. The ferroelectricity can be treated as a problem of lattice dynamics. It is a big step in establishing a unified theory. The basic idea behind the approach is relatively simple. In the ideal case of zero damping the dielectric constant of a crystal can be written in a general form [6].

$$\in(\omega)=\in_\infty+\sum\frac{b_i^2}{\omega_i^2-\omega^2}$$

Where $\in_\infty$ is high frequency (optical dielectric constant and the summation index i refers the ith optical mode of lattice vibration, ω_i^2 measures the strength of the restoring force and b_i^2 the strength of the coupling between the I vibrational mode to the electric field. According to Eq. (3.16) the static dielectric constant can be written as

$$\in_s = \in_\infty + \sum_i \frac{b_i^2}{\omega_i^2}$$

When the restoring force of one of the vibrational modes of lattice becomes very small at a given temperature, the static dielectric constant can become very large.

From the well known Szigeti relation and its other form defined in the book [14], one can define

$$\frac{M\omega_t^2}{r} = 1 - \frac{(\in_\infty + 2 \in_0) N(Ze)^2}{(3 \in_0)^2 r} = \eta(T - T_c)$$

By expanding the temperature dependence of certain atomic parameters into a Taylor's series at $T=T_c$ and where an effective ionic charge of Ze is assumed for sake of generality.

Simplifying applying advance theory of dielectrics [4], one can have

$$\in_s - \in_\infty = \frac{(\in_s + 2 \in_0)(\in_\infty + 2 \in_\infty)}{(3 \in_0)^2} \frac{N(Ze)^2}{r\eta(T - T_c)}$$

Eq. (3.19) is known as Curie-Weiss Law.

The condition for ferroelectricity ($(\in_s \to \infty)$ requires $T=T_c$ in the equation which in turn requires $\omega_1 \to 0$.

Therefore the theory of ferroelectricity is intimately connected with the theory of lattice Dynamics.

The condition for $\omega_t = 0$ from Ed. (3.18) can be written as

$$\frac{N(Ze)^2}{3\in_0 r} = 1 - \frac{\in_\infty - \in_0}{\in_\infty + 2\in_0} = 1 - \frac{N(\alpha_+ + \alpha_-)}{3\omega_0}$$

Realizing that $(Ze)^2/r$ is the ionic polarizability α_i at zero frequency, the equation gives

$$N(\alpha_i + \alpha_e)/3\in_0 = 1$$

Therefore the condition for polarizability catastrophe and the condition for $\omega_t = 0$ are the same.

2.1.7 ADVANCE THEORY

Based on Ginzburg–Landau theory, the free energy of a ferroelectric material, in the absence of an electric field and applied stress may be written as a Taylor expansion in terms of the order parameter, *P* [7]. If a sixth order expansion is used (i.e. 8th order and higher terms truncated), the free energy is given by:

$$\begin{aligned}\Delta G = \; & \tfrac{1}{2}\alpha_0 (T - T_0)\left(P_x^2 + P_y^2 + P_z^2\right) + \tfrac{1}{4}\alpha_{11}\left(P_x^4 + P_y^4 + P_z^4\right) \\ & + \tfrac{1}{2}\alpha_{12}\left(P_x^2 P_y^2 + P_y^2 P_z^2 + P_z^2 P_x^2\right) \\ & + \tfrac{1}{6}\alpha_{111}\left(P_x^6 + P_y^6 + P_z^6\right) \\ & + \tfrac{1}{2}\alpha_{112}\left[P_x^4\left(P_y^2 + P_z^2\right) + P_y^4\left(P_x^2 + P_z^2\right) + P_z^4\left(P_x^2 + P_y^2\right)\right] \\ & + \tfrac{1}{2}\alpha_{123} P_x^2 P_y^2 P_z^2\end{aligned}$$

where P_x, P_y, and Pz are the components of the polarization vector in the *x, y,* and *z* directions respectively, and the coefficients, α_i, α_{ij}, α_{ijk} must be consistent with the crystal symmetry. To investigate domain formation and other phenomena in ferroelectrics, these equations are often used in the context of a phase field model. Typically, this involves adding a gradient term, an electrostatic term and an elastic term to the free energy. The equations are then discretized onto a grid using the finite difference method and solved subject to the constraints of Gauss's law and Linear elasticity.

In all known ferroelectrics, $\alpha_0 > 0$ and $\alpha_{111} > 0$. These coefficients may be obtained experimentally or from ab-initio simulations. For ferroelectrics with a first order phase transition, $\alpha_{11} < 0$ and $\alpha_{11} > 0$ for a second order phase transition.

The spontaneous polarization, P_s of a ferroelectric for a cubic to tetragonal phase transition may be obtained by considering the 1D expression of the free energy which is:

$$\Delta G = \frac{1}{2}\alpha_0 \left(T - T_0\right) P_x^2 + \frac{1}{4}\alpha_{11} P_x^4 + \frac{1}{6}\alpha_{111} P_x^6$$

This free energy has the shape of a double well potential with two free energy minima at $P = \pm P_s$, where P_s is the spontaneous polarization. At these two minima, the derivative of the free energy is zero, i.e.:

$$\frac{\partial \Delta G}{\partial P_x} = \alpha_0 \left(T - T_0\right) P_x + \alpha_{11} P_x^3 + \alpha_{111} P_x^5 = 0$$

$$P_x \left[\alpha_0 \left(T - T_0\right) + \alpha_{11} P_x^2 + \alpha_{111} P_x^4\right] = 0$$

Since $P_x = 0$ corresponds to a free energy maxima in the ferroelectric phase, the spontaneous polarization, P_s, is obtained from the solution of the equation:

$$\alpha_0 \left(T - T_0\right) + \alpha_{11} P_x^2 + \alpha_{111} P_x^4 = 0$$

which is:

$$P_s^2 = \frac{1}{2\alpha_{111}} \left[-\alpha_{11} \pm \sqrt{\alpha_{11}^2 - 4\alpha_0 \alpha_{111} \left(T - T_0\right)}\right]$$

and elimination of solutions yielding a negative square root (for either the first or second order phase transitions) gives:

$$P_s = \sqrt{\frac{1}{2\alpha_{111}} \left[-\alpha_{11} + \sqrt{\alpha_{11}^2 - 4\alpha_0 \alpha_{111} \left(T - T_0\right)}\right]}$$

If $\alpha_{111} = 0$, using the same approach as above, the spontaneous polarization may be obtained as:

$$P_s = \sqrt{-\frac{\alpha_0 \left(T - T_0\right)}{\alpha_{11}}}$$

The hysteresis loop (P_x versus E_x) may be obtained from the free energy expansion by adding an additional electrostatic term, $E_x P_x$, as follows:

$$\Delta G = \frac{1}{2}\alpha_0 (T - T_0) P_x^2 + \frac{1}{4}\alpha_{11} P_x^4 + \frac{1}{6}\alpha_{111} P_x^6 - E_x P_x$$

$$\frac{\partial \Delta G}{\partial P_x} = \alpha_0 (T - T_0) P_x + \alpha_{11} P_x^3 + \alpha_{111} P_x^5 - E_x = 0 \qquad (3.30)$$

$$E_x = \alpha_0 (T - T_0) P_x + \alpha_{11} P_x^3 + \alpha_{111} P_x^5$$

Plotting E_x as a function of P_x and reflecting the graph about the 45 degree line gives an 'S' shaped curve. The centre part of the 'S' corresponds to a free energy local maximum (since $\frac{\partial^2 \Delta G}{\partial P_x^2} < 0$). Elimination of this region, and connection of the top and bottom portions of the 'S' curve by vertical lines at the discontinuities gives the hysteresis loop.

2.1.8 APPLICATIONS

The nonlinear nature of ferroelectric materials can be used to make capacitors with tunable capacitance. Typically, a ferroelectric capacitor simply consists of a pair of electrodes sandwiching a layer of ferroelectric material. The permittivity of ferroelectrics is not only tunable but commonly also very high in absolute value, especially when close to the phase transition temperature. This fact makes ferroelectric capacitors small in size compared to dielectric (non-tunable) capacitors of similar capacitance.

The spontaneous polarization of ferroelectric materials implies a hysteresis effect which can be used as a memory function. Indeed, ferroelectric capacitors are used to make ferroelectric RAM [18] for computers and RFID cards. These applications are usually based on thin films of ferroelectric materials as this allows the high coercive field required to switch the polarization to

be achieved with a moderate voltage, though a side effect of this is that a great deal of attention needs to be paid to the interfaces, electrodes and sample quality for devices to work reliably [19]. All ferroelectrics are required by symmetry considerations to be also piezoelectric and pyroelectric. The combined properties of memory, piezoelectricity, and pyroelectricity make ferroelectric capacitors very useful, e.g. for sensor applications. Ferroelectric capacitors are used in medical ultrasound machines (the capacitors generate and then listen for the ultrasound ping used to image the internal organs of a body), high quality infrared cameras (the infrared image is projected onto a two dimensional array of ferroelectric capacitors capable of detecting temperature differences as small as millionths of a degree Celsius), fire sensors, sonar, vibration sensors, and even fuel injectors on diesel engines. As well, the electro-optic modulators that form the backbone of the Internet are made with ferroelectric materials.

One new idea of recent interest is the *ferroelectric tunnel junction* (*FTJ*) in which a contact made up by nanometer-thick ferroelectric film placed between metal electrodes. The thickness of the ferroelectric layer is thin enough to allow tunneling of electrons. The piezoelectric and interface effects as well as the depolarization field may lead to a giant electroresistance (GER) switching effect.

Another hot topic is multiferroics, where researchers are looking for ways to couple magnetic and ferroelectric ordering within a material or heterostructure; there are several recent reviews on this topic [20-23]. Cross-section

3.1 EXPERIMENTAL

Human endeavor towards continuous improvement in the quality of life has resulted in a host of advance materials and new technologies. There is a wide variety of the behavior of materials, but a great chasm exists between the experimental results and the ability of the theoretician to predict these results. Of course, the serious experimentalist has the upper hand in this game, since he reports the newer phenomena. Accuracy of the experimental results depends on seriousness of experimenter and sophistication of instruments.

Silicon

Silicon, a tetravalent metalloid, is a chemical element with the symbol **Si** and atomic number 14. Silicon is the eighth most common element in the universe by mass, but very rarely occurs as the pure free element in nature. It is most widely distributed in dusts, sands, planetoids, and planets as various forms of silicon dioxide (silica) or silicates. Most silicon is used commercially without being separated, and indeed often with little processing of compounds from nature. Although most free silicon is used in the steel refining, aluminum-casting, and fine chemical industries (often to make fumed silica), the relatively small portion of very highly purified silicon that is used in semiconductor electronics (< 10%) is perhaps even more critical.

Name, symbol,number	silicon, Si, 14
Element category	metalloid
Group, period,block	14, 3, p
Standard atomic weight	28.085(1)
Electron configuration	[Ne] $3s^2$ $3p^2$
Phase	solid
Density(near r.t.)	2.3290 $g \cdot cm^{-3}$
Liquid density atm.p.	2.57 $g \cdot cm^{-3}$
Melting point	1687 K, 1414 °C, 2577 °F
Boiling point	3538 K, 3265 °C, 5909 °F
Heat of fusion	50.21 $kJ \cdot mol^{-1}$
Heat of vaporization	359 $kJ \cdot mol^{-1}$
Molar heat capacity	19.789 $J \cdot mol^{-1} \cdot K^{-1}$

Indium

Indium is a chemical element with symbol In and atomic number 49. This rare, very soft, malleable and easily fusible post transition metal is chemically similar to galliumand thallium, and shows intermediate properties between these two. Indium's current primary application is to form transparent electrodes from indium tin oxide (ITO) in liquid crystal displays and touchscreens, and this use largely determines its global mining production. It is widely used in thin-films to form lubricated layers. Indium is not known to be used by any

organism. In a similar way to aluminium salts, indium(III) ions can be toxic to the kidney when given by injection, but oral indium compounds do not have the chronic toxicity of salts of heavy metals, probably due to poor absorption in basic conditions. Radioactive indium-111 (in very small amounts on a chemical basis) is used in nuclear medicine tests, as a radiotracer to follow the movement of labeled proteins and white blood cells in the body.

Name, symbol,number	indium, In, 49
Pronunciation	/□ɪ ndiəm/ ***ɪn-dee-əm***
Element category	post-transition metal
Group, period,block	13, 5, p
Standard atomic weight	114.818
Electron configuration	[Kr] $4d^{10}\ 5s^2\ 5p^1$
Phase	solid
Density(near r.t.)	7.31 $g{\cdot}cm^{-3}$
Liquid density atm.p.	7.02 $g{\cdot}cm^{-3}$
Melting point	429.7485 K, 156.5985 °C, 313.8773 °F
Boiling point	2345 K, 2072 °C, 3762 °F
Heat of fusion	3.281 $kJ{\cdot}mol^{-1}$
Heat of vaporization	231.8 $kJ{\cdot}mol^{-1}$
Molar heat capacity	26.74 $J{\cdot}mol^{-1}{\cdot}K^{-1}$

Doping semiconductor

In semiconductor production, **doping** intentionally introduces impurities into an extremely pure (also referred to as *intrinsic*) semiconductor for the purpose of modulating its electrical properties. The impurities are dependent upon the type of semiconductor. Lightly and moderately doped semiconductors are referred to as *extrinsic*. A semiconductor doped to such high levels that it acts more like a conductor than a semiconductor is referred to as *degenerate*.

Carrier concentration

The concentration of dopant introduced to an intrinsic semiconductor determines its concentration and indirectly affects many of its electrical properties. The most important factor that doping directly affects is the material's carrier concentration. In an intrinsic semiconductor under thermal equilibrium, the concentration of electrons and holes is equivalent. That is,

$$n = p = n_i.$$

If we have a non-intrinsic semiconductor in thermal equilibrium the relation becomes:

$$n_0 \cdot p_0 = n_i^2$$

Where n_0 is the concentration of conducting electrons, p_0 is the electron hole concentration, and n_i is the material's intrinsic carrier concentration. Intrinsic carrier concentration varies between materials and is dependent on temperature. Silicon's n_i, for example, is roughly 1.08×10^{10} cm^{-3} at 300 kelvin (room temperature).[4]

In general, an increase in doping concentration affords an increase in conductivity due to the higher concentration of carriers available for conduction. Degenerate (very highly doped) semiconductors have conductivity levels comparable to metals and are often used in modern integrated circuits as a replacement for metal. Often superscript plus and minus symbols are used to denote relative doping concentration in semiconductors. For example, n^+ denotes an n-type semiconductor with a high, often degenerate, doping concentration. Similarly, p^- would indicate a very lightly doped p-type material. Even degenerate levels of doping imply low concentrations of impurities with respect to the base semiconductor. In crystalline intrinsic silicon, there are approximately 5×10^{22} atoms/cm^3. Doping concentration for silicon semiconductors may range anywhere from 10^{13} cm^{-3} to 10^{18} cm^{-3}. Doping concentration above about 10^{18} cm^{-3} is considered

degenerate at room temperature. Degenerately doped silicon contains a proportion of impurity to silicon on the order of parts per thousand. This proportion may be reduced to parts per billion in very lightly doped silicon. Typical concentration values fall somewhere in this range and are tailored to produce the desired properties in the device that the semiconductor is intended for.

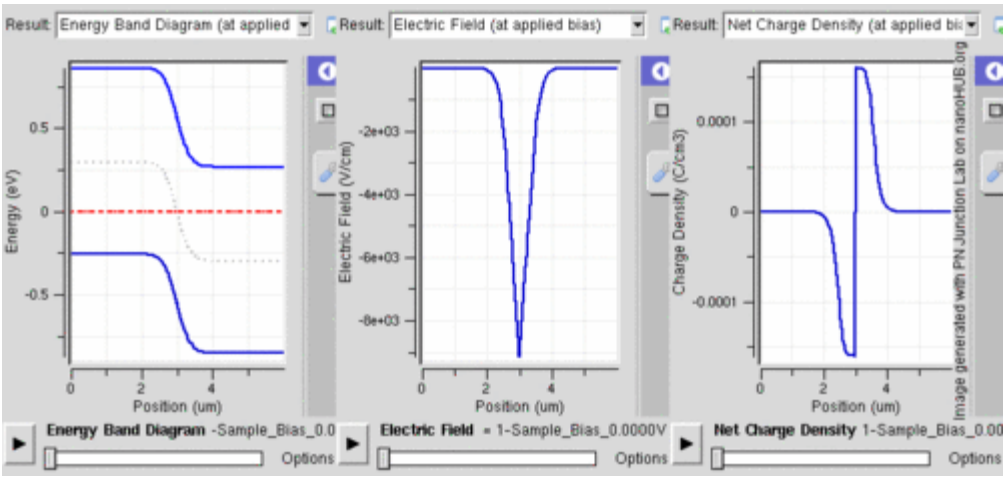


Fig.3.1

Band diagram of PN junction operation in forward bias mode showing reducing depletion width. Both p and n junctions are doped at a $1\times10^{15}/cm^3$ doping level, leading to built-in potential of ~0.59 V. Reducing depletion width can be inferred from the shrinking charge profile, as fewer dopants are exposed with increasing forward bias [1].

Doping a semiconductor crystal introduces allowed energy states within the band gap but very close to the energy band that corresponds to the dopant type. In other words, donor impurities create states near the conduction band while acceptors create states near the valence band. The gap between these energy states and the nearest energy band is usually referred to as dopant-site bonding energy or $E_B$and is relatively small. For example, the E_B for boron in silicon bulk is 0.045 eV, compared with silicon's band gap of about 1.12 eV. Because E_B is so small, it takes little energy to ionize.

Apparatus used in the experiment:

1. Micro-oven: capacity 20ltrs, power 4048GW

Fig.3.2: micro oven

2. Wheat powder

3. Sample: Silicon(single crystal)(111) plane

Indium

4. Variable resister:

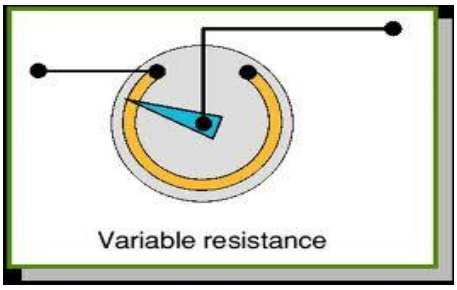


Fig.3.3: variable Resister

A variable resistor is usually a long coiled wire with hundreds of turns. It is also known by the name of rheostat. Actually, all wires have resistance. You can make a variable resistor out of any

material. What happens is that there is a sliding contact along the length of the coil. One end provides the least resistance while the other end provides the maximum resistance. This is so because in the second case, electricity has to go through the entire wire coil and hence there is greater resistance to it. You can get the desired level of resistance from the resistor by sliding the contacts.

5. Battery. 9 volt

6. Multimeter: As the name suggests, multimeters are those measuring instruments which can be used to calculate multiple circuit characteristics. Making them digital gives highly precise outputs as unlike their analog counterparts, there is no needle whose pointer is to be figured out. How are the digital meters more advanced than their predecessor? What internal circuitry is there to power such quick and rapid calculations? Just simply hook it to the circuit and take readings on the fly? Multimeter does that for us. So let us explore the Nitty Gritties of the Multimeter that make it a jack of many (if not all) trades of electrical measurements.

Fig3.4: multimeter

Working Principle:

We have tested 4 silicon samples. First we studied the properties of normal silicon sample. Secondly a silicon sample is heated for 3 minutes inside the micro-oven. Third silicon sample is heated with Indium doping for 3 minutes. Fourth sample is heated for 5 minutes with Indium doped.

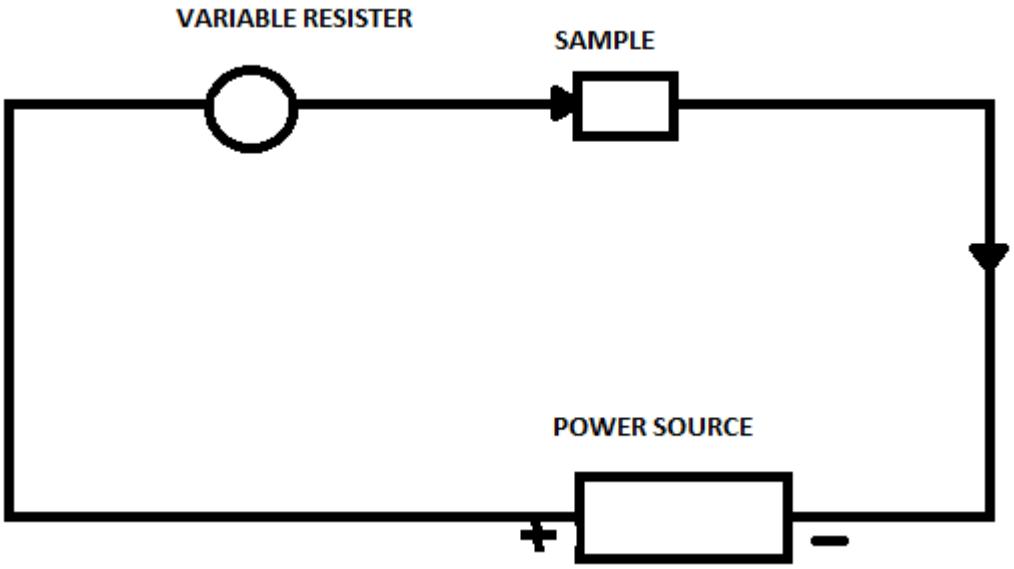


Fig.3.5: circuit diagram of to measure the V-I characteristic

As shown in the figure the current is taken from the power source, then it goes to the variable register to get required amount of current. Then using different samples are used. After that we calculate the voltage drop by using multmeter.

Indium doped silicon has been grown from indium – rich solutions using a gradient – transport solution growth process. The growth temperatures were varied from 150^0c to 200^0c inside a micro-oven to determine the voltage drop of indium in silicon. The indium concentration obtainedin silicon. The growth process is described by one-dimensional diffusion .The solution – grown crystals were found to have a lower concentration of this shallower defect than melt grown crystals of the same indium concentration. The Oxygen and carbon concentrations are less because the sample is heated inside the microoven. Cross-section

RESULTS AND DISCUSSION

V-I characteristics:

Indium doped silicon has been grown from indium – rich solutions using a gradient – transport solution growth process. The growth temperatures were varied from 150^0c to 200^0c inside a micro-oven to determine the voltage drop of indium in silicon. The indium concentration obtained in silicon. The growth process is described by one-dimensional diffusion .The solution –grown crystals were found to have a lower concentration of this shallower defect than melt grown crystals of the same indium concentration. The Oxygen and carbon concentrations are less because the sample is heated inside the microoven. Cross-section

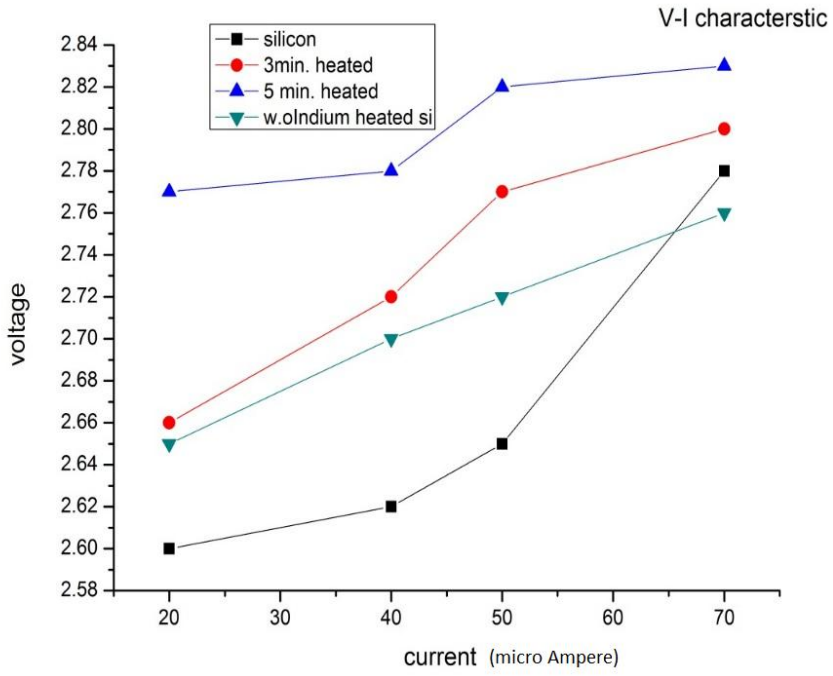


Fig.4.1: V-I Characteristic

From the graph it is concluded that:

- The SQUARE line shows the voltage drop of silicon in normal condition.
- The ARROW line shows the variation of voltage drop when heated without doping
- The CIRCLED line shows voltage drop with Indium doped when heated for 3 minutes.
- The TRIANGLE line shows the voltage drop with indium doped when heated for 5 minutes.

From the above figure it is found that there is a sharp voltage drop of Silicon without In doping. But for the sample after doping with In and heated in micro-oven the voltage drop is different, i.e. there is sharp drop of voltage between 40-50 µA current range. Which is more essential for semiconductor devices.

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XRD Analysis

From the experiment it is found that after indium doping there is a compound Peak formed ($BaMnSiO_4$,$Cs_2Si_2O_5$).this is the difference found after Indium doping on silicon inside the micro oven.

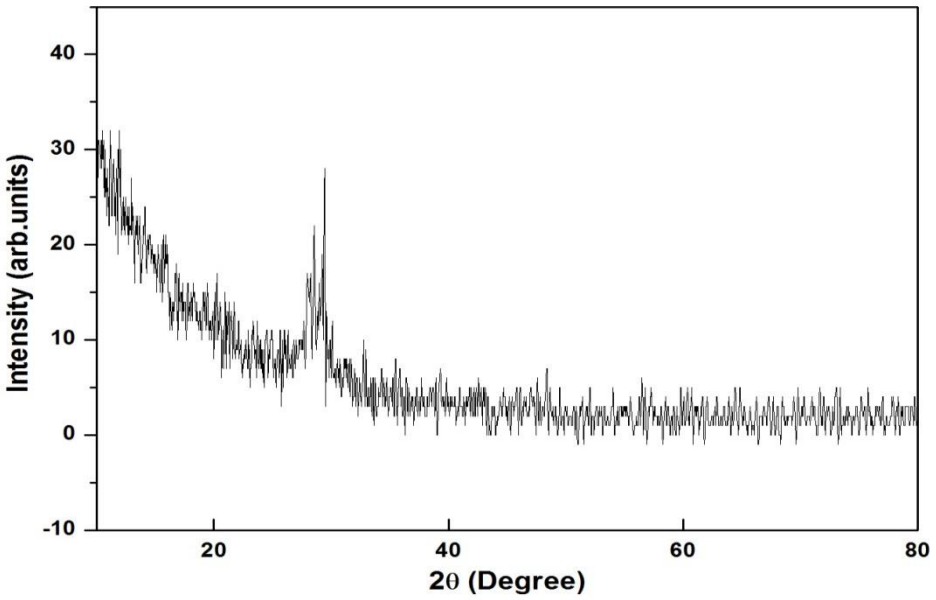

Fig 4.2 (a) Si single crystal

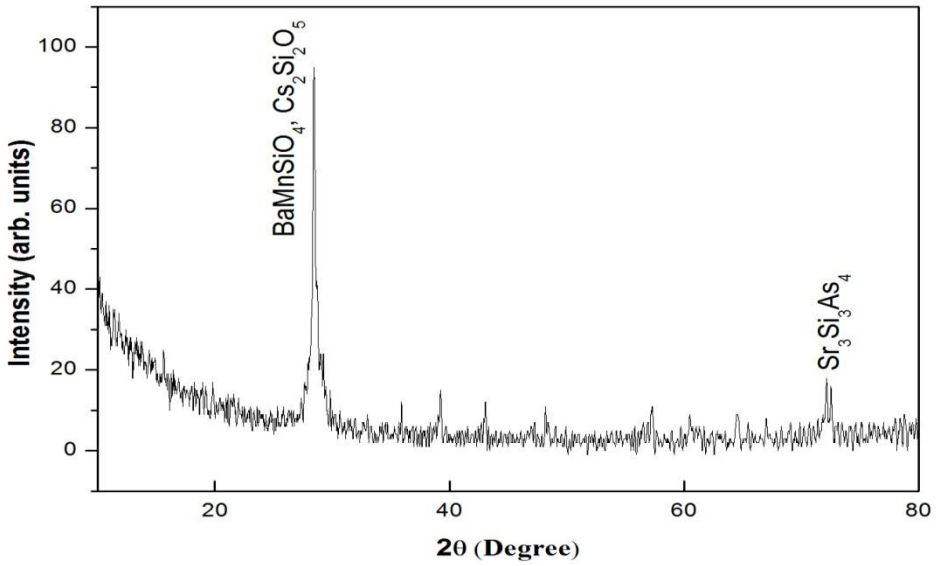

Figure 4.2(b) Si doped with Indium

The XRD analysis of the samples are shown in figure4.2 and 4.2a shows the silicon peak.Where as the samples after doping with indium figure4.2(b)exhibits the formation of $SrSiSs_4$,$BaMnSiO_4$ and $Cs_2Si_2O_6$phases.These phases might be responsible for change in V-I characterstic than that of silicon crystal.

SEM Analysis

Precipitation in grain observed in SEM view. That may be responsible for Voltage drop in the Indium doped Silicon sample.

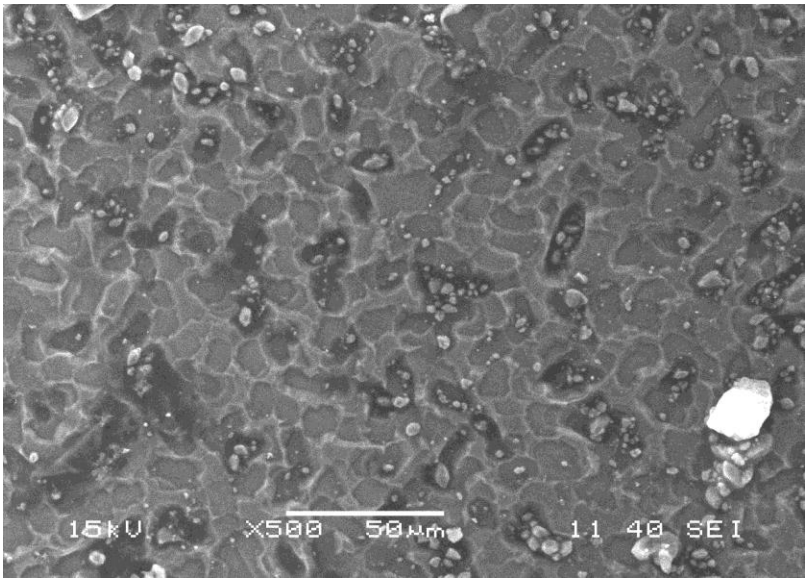

Figure4.3: Microstructure of a silicon single crystal

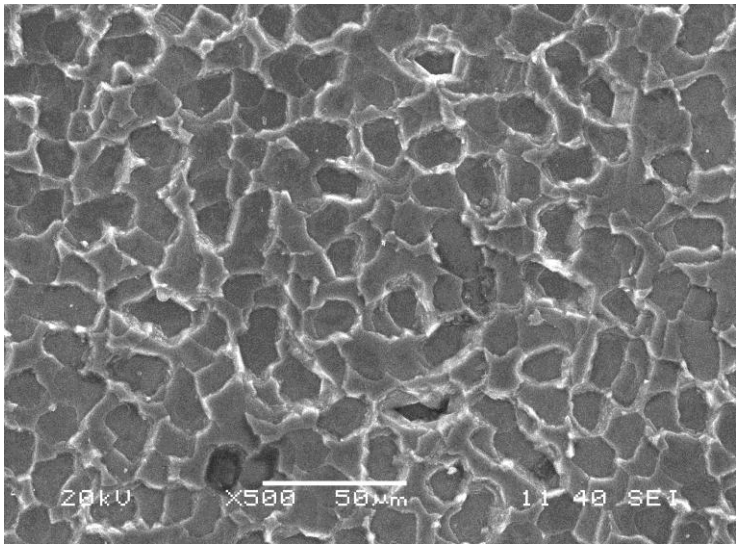

Fig.4.4(a)

Microstructure of a silicon single crystal after 3 min. heating.

From the above structure it is found that there are some precipited single crystal without treatment .after heating 3 min inside the micro-oven no precipited is found that is homogenize structure is obtained.

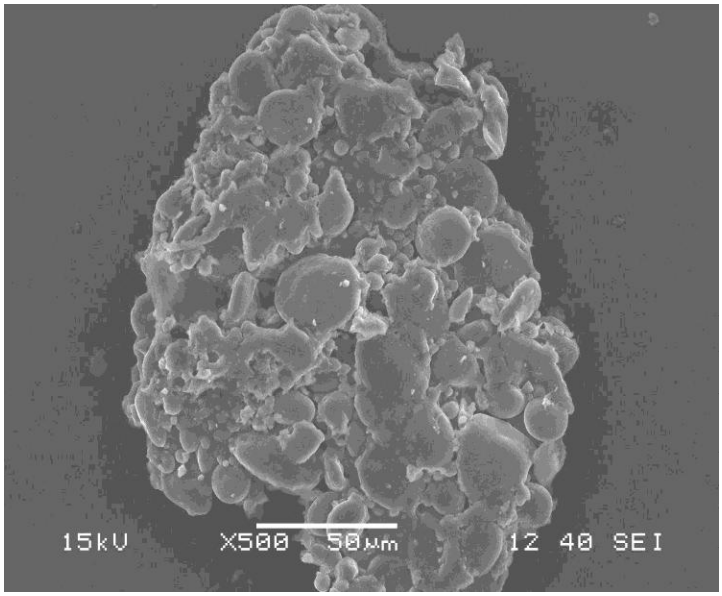

Fig 4.4(b)

Figure shows that after 3minutes heated inside the micro-oven, white spot shows Indium and the black spot is the silicon. There is no crystal structure comes for silicon.

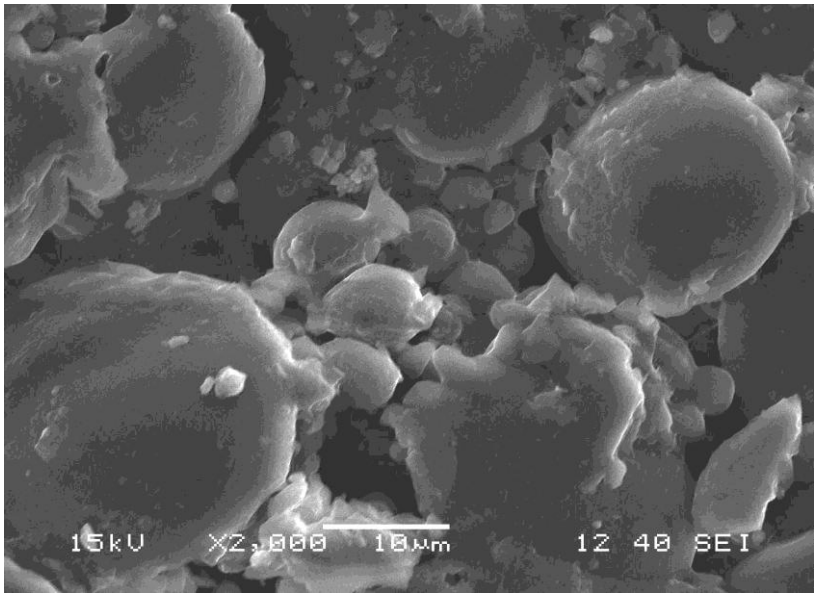

Fig.4.5:

Fig 4.5 shows the micro structure after doping globular precipitate seen may be the phase form as observed in XRD.

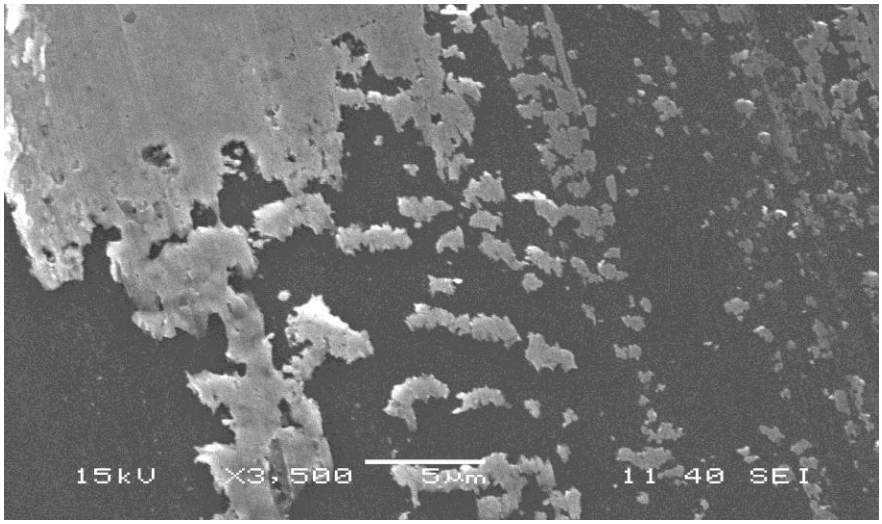

Fig 4.6

Fig 4.6 shows the micro structure of sample after heating 5 minute inside the micro oven it typical magnified view of the surface. It shown in figure 4.7. It can be visualized the its shape and size become elongated may be due to growth and coalescences of the particle.

The variation in the PI characteristics in Indium 2 and un dope sample for different time is due to the observed structural changes.

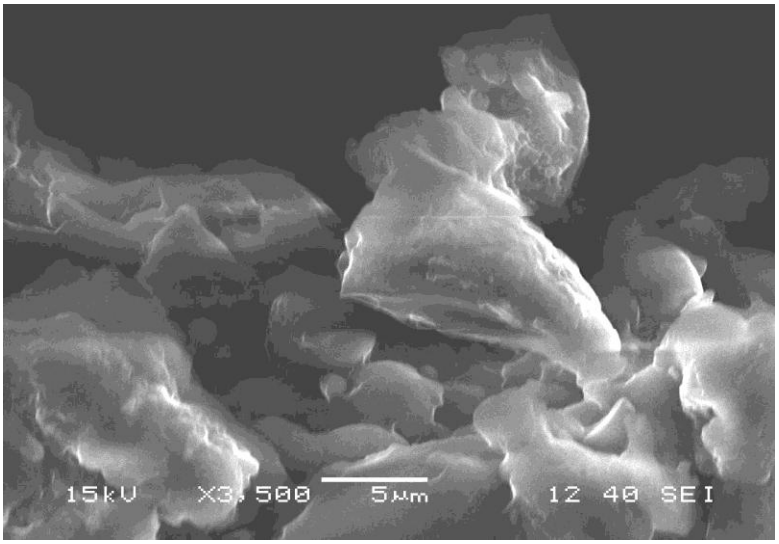

Fig.4.7

Figure 4.7 shows after 3 minutes heated inside the micro-oven, and magnifying 3500,It is found that the white spots are Indium and the black spots are Silicon.

CONCLUSION

From the investigation it can be concluded that:

1. There is a maximum voltage drop in between 40 – 50 micro-ampere in indium doped silicon metal which is heated for 3-5 minutes.

2. In XRD analysis we have found that there is a peak difference comes when an indium doped silicon metal is heated.

3. Precipitation in grain observed in SEM view. That may be responsible for Voltage drop in the Indium doped Silicon sample.

FUTURE WORK

1. Different concentration of indium doping may carried out to study V-I characteristics.
2. 2. Different heating time may be done.
3. Different dose of the indium doping can be made.
4. Effect of temperature in solubility may study.

REFERENCE

[1] Resistance www.wikipedia.com

[2] W. Cochran, *Phy. Rev. Lett.* 3 (1959) 412.

[3] D. Henning, A. Schnell, G. Simon, *J. Am. Ceram. Soc*., 65 (1982) 539.

[4] Z. Yu, R. Guo, A. S. Bhalla, *J.Appl. Phys,* 88 (2000) 410.

[5] S. Lee, T. Son, J. Yun, H. Kwon, G. L. Messing, B. Jun, *Mat. Lett.* 28 (2004) 2932.

[6] A. Testinon, M. T. Buscaglia, M. Viviani, V. Buscaglia, P. Nanni, *J. Am. Ceram. Soc*., 87 (2008) 79.

[7] W. Xiao, X. Gang, R. Zhaohui, S. Ge, H. Georong, *J. Am. Ceram. Soc*., 91 (2008) 3774.

[8] S. P. Singh, M. K. Bagde, Quantum Mechanics (S. Cand & Company Ltd., New Delhi , 1992), p.131.

[9] J. R. Chelikowsky, Encyclopedia of Condensed Matter Physics in: F. Bassani, G. L. Liedl,P. Wyder (Eds.), (Oxford, 2005), p. 51.

[10] C. Suryanarayana, C.C. Koch in: C. Suryanarayana, (Ed.), Non-Equilibrium Processing Of Materials (Pergamon, New York, 1999), p. 313–344

[11] W. Känzig, *Ferroelectrics and Antiferroelectrics* in F. Seitz, T. P. Das, D. Turnbull, E. L Hahn, *Solid State Physics*. **4**. (Academic Press, 1957) p.5.

[12] M. Lines, A. Glass, *Principles and applications of ferroelectrics and related materials* (Clarendon Press, Oxford, 1979).

[13] J. Valasek, *Phys. Rev.* **17** (1921) 475.

[14] B. S. Saxena, R. C. Gupta, P. N. Saxena, *Fundamentals of Solid State Physics* (Pragati Prakashan, Meerut, 1995) p.626.

[15] M. Born, K. Huang, *Dynamic Theory of Crystal Lattice* (Clarenden Press, Oxford, 1954).

[16] Ferroelectricity, *www.wikipedia.com*

[17] J. F. Scott, *Ferroelectric Memories* (Springer, 2000).

[18] M. Dawber, K.M. Rabe, J.F. Scott, *Rev. Mod. Phys.* **77** (2005) 1083.

[19] R. Ramesh, N.A Spaldin, *Nature Mat.* **6** (2007) 21.

[20] W. Eerenstein, N.D. Mathur, J.F. Scott, *Nature* **442** (2006) 759.

[21] N.A. Spaldin, M. Fiebig, *Science* **309** (2005) 5391.

[22] M. Fiebig *J. Phys. D: Appl. Phys.* **38** (2005) R123.

■■■

A Study of Processing of Indium Doped Semiconductor Material.

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE

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Rama Chandra Sarangi

Roll No. 211MM1369

Department of Metallurgical & Materials Engineering

National Institute of Technology

Rourkela

2011-2013

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CONTENTS

ABSTRACT

Indium- doped Silicon is being investigated as an extrinsic photoconductor material for use in the 3 to 5 μm infrared region. The low indium concentration obtained by standard growth methods and presence of a shallower defect level associated with the indium. The concentration of indium in float zone grown crystals is generally even lower than this because of the low segregation co-efficient of indium.

A shallower defect Centre associated with indium and labelled as indium. It is observed that in Hall co-efficient measurements at energy of about 0.11eV.

Solution growth techniques such as gradient –transport solution growth and LPE have been used to grow III – V compound. The use of temperature – gradient zone melting as a means of producing large area p – n junctions in silicon. An important feature of this solution growth procedure is that the crystals are grown the melting point of silicon.so the retrograde solubility of the impurities can be used to obtain very heavily doped crystals.

In the present work Indium is doped on silicon metal inside a micro-oven at the temperature of 200^0C.Different samples are kept inside the micro-oven for different time period. After that XRD,SEM and V-I characteristics have been done, then voltage drop is calculated and different peaks have come and changes in micro structure have been found.

INTRODUCTION

The modern concept of electrical resistance was first discovered by G. S. Ohm, in 1926, who formulated the famous equation: V=IR, while working on direct-current circuit. The resistance is a function of temperature and stress for a given material. This property of resistance is employed in resistance-temperature conversion.

1.1 RESISTANCE AND ITS ORIGIN:

The electrical resistance of an object is a measure of its opposition to the passage of an electric current. Electrical resistance of a circuit component or device is defined as the ratio of the voltage applied to the electric current which flows through it.

I V R □

The SI unit of electrical resistance is the ohm (Ω). Resistance's reciprocal quantity is electrical conductance measured in siemens.

1.1.1 Causes of resistance:

In metals:

When an electrical potential difference (a voltage) is applied across the metal, the electrons drift from one end of the conductor to the other, under the influence of the electric field. Near room temperatures, the thermal motion of ions is the primary source of scattering of electrons (due to destructive interference of free electron waves on non-correlating potentials of ions), and is thus the prime cause of metal resistance. Imperfections of lattice also contribute into resistance, 10 although their contribution in pure metals is negligible. The longer the conductor, the more scattering events occur in each electron's path through the material, so the higher the resistance [1].

In semiconductor and insulator:

In semiconductors the position of the Fermi level is within the band gap, approximately half-way between the conduction band minimum and valence band maximum for intrinsic (undoped) semiconductors. This means that at zero kelvin, there are no free conduction electrons and the resistance is infinite. However, the resistance will continue to decrease as the charge carrier density in the conduction band increases. In extrinsic (doped) semiconductors, dopant atoms increase the majority charge carrier concentration by donating electrons to the conduction band or accepting holes in the valence band. For both types of donor or acceptor atoms, increasing the dopant density leads to a reduction in the resistance. Highly doped semiconductors hence behave like metallic. At very high temperatures, the contribution of thermally generated carriers will dominate over the contribution from dopant atoms and the resistance will decrease exponentially with temperature [1].

1.1.2 Temperature dependence of resistance:

Near room temperature, the electrical resistance of a typical metal increases linearly with increase in temperature, while the electrical resistance of a typical semiconductor decreases with rising temperature. To the first order, the temperature dependence of resistance follows the relation

where, T is its temperature, $T0$ is a reference temperature (usually zero Kelvin or room temperature), R_0 is the resistance at $T0$, and α is the coefficient of change in resistivity per unit temperature also known as, temperature coefficient of resistance. The constant α depends only on the material being considered.

Intrinsic semiconductors become better conductors as the temperature increases; the electrons are jumped to the conduction energy band by thermal energy, where they flow freely and in doing so leave behind holes in the valence band which also flow freely. The electric resistance of a typical intrinsic (non-doped) semiconductor decreases exponentially with rise temperature:

Extrinsic (doped) semiconductors have a far more complicated temperature profile. As temperature increases starting from absolute zero, they first decrease steeply in resistance as the carriers leave the donors or acceptors. At higher temperatures it will behave like intrinsic semiconductors as the carriers from the donors/acceptors become insignificant compared to the thermally generated carriers[1].

1.2 RESISTIVITY

The quantitative measure of a material‟s opposition to the flow of current is called resistivity. It depends only on the composition of the material and not on the shape and size.

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where: R is the resistance(ohms), ρ is resistivity(ohm-meters), L is the length(meters), and A is the cross-sectional area(square-meters).

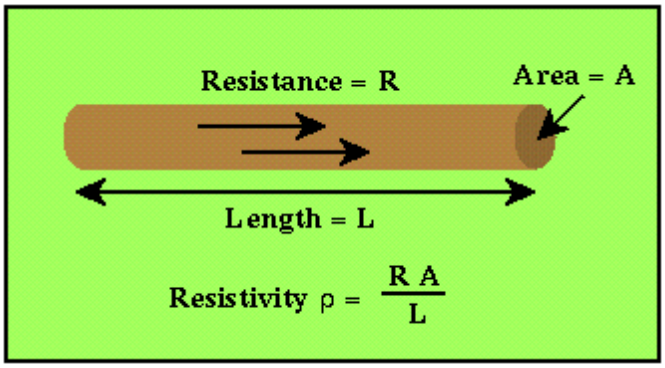


Fig 1.1: Resistivity of a material [3]

Although the resistivity is temperature dependent, it can be used to calculate the resistance of a wire of given geometry at a given temperature.

The resistivity of the material changes with temperature. For many materials, the change is a simple linear function of temperature: , where: ρ(T) = resistivity at temperature T, ρ_0 =resistivity at temperature T0, α =temperature coefficient of resistivity [4].

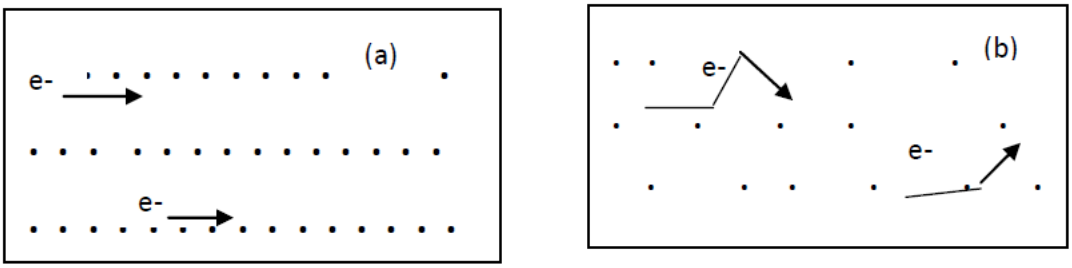


Fig 1.2: movement of electron in (a) cold body (b) hot body. In cold body, the ions are more ordered and the electrons move without much scattering. In hot body, due to vibration of ions, the electrons undergo more scattering.

Materials	Resistivity, ρ(ohm-meter)
Metals	10−8
Semiconductors	Variable
Electrolytes	Variable
Insulators	1016
Superconductors	0(exactly)

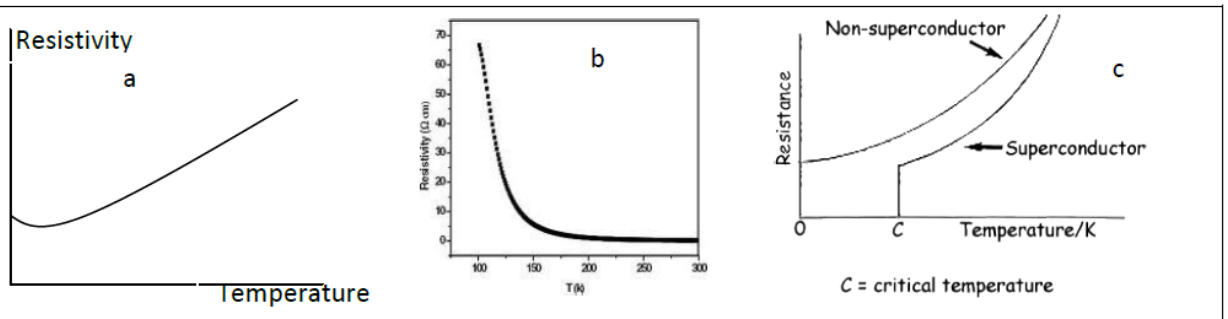


Fig 1.3: Resistivity vs. temperature plot for a) metal b) semiconductor c) superconductor

Table 1.1 shows the resistivity of the various materials. The temperature dependent of resistivity of the various materials as shown in Figure 1.3.

1.3 MATERIALS DESCRIPTION

Silicon, a tetravalent metalloid, is a chemical element with the symbol **Si** and atomic number 14. It is less reactive than its chemical analog carbon, the nonmetal directly above it in the periodic table, but more reactive than germanium, the metalloid directly below it in the table. It was first prepared and characterized in pure form in 1823. In 1808, it was given the name silicium (from Latin: *silicis*, flints), with an **-ium** word-ending to suggest a metal, a name which the element retains in several non-English languages. However, its final English name, first suggested in 1817, reflects the more physically similar elements carbon and boron.

Silicon is the eighth most common element in the universe by mass, but very rarely occurs as the pure free element in nature. It is most widely distributed in dusts, sands, planetoids, and planets as various forms of silicon dioxide (silica) or silicates. Over 90% of the Earth's crust is composed of silicate minerals, making silicon the second most abundant element in the Earth's crust (about 28% by mass) after oxygen.

Most silicon is used commercially without being separated, and indeed often with little processing of compounds from nature. These include direct industrial building-use of clays, silica sand and stone. Silica is used in ceramic brick. Silicate goes into Portland cement for mortar and stucco, and when combined with silica sand and gravel, to make concrete. Silicates are also in whiteware ceramics such as porcelain, and in traditional quartz-based soda-

lime glass. More modern silicon compounds such as silicon carbide form abrasives and high-strength ceramics. Silicon is the basis of the ubiquitous synthetic silicon-based polymers called silicones.

Elemental silicon also has a large impact on the modern world economy. Although most free silicon is used in the steel refining, aluminum-casting, and fine chemical industries (often to make fumed silica), the relatively small portion of very highly purified silicon that is used in semiconductor electronics (< 10%) is perhaps even more critical. Because of wide use of silicon in integrated circuits, the basis of most computers, a great deal of modern technology depends on it.

Silicon is an essential element in biology, although only tiny traces of it appear to be required by animals. However, various sea sponges as well as microorganisms like diatoms need silicon in order to have structure. It is much more important to the metabolism of plants, particularly many grasses.

Indium is a chemical element with symbol **In** and atomic number 49. This rare, very soft, malleable and easily fusible post-transition metal is chemically similar to gallium and thallium, and shows intermediate properties between these two. Indium was discovered in 1863 and named for the indigo blue line in its spectrum that was the first indication of its existence in zinc ores, as a new and unknown element. The metal was first isolated in the following year. Zinc ores continue to be the primary source of indium, where it is found in compound form. Very rarely the element can be found as grains of native (free) metal, but these are not of commercial importance.

Indium's current primary application is to form transparent electrodes from indium tin oxide (ITO) in liquid crystal displays and touchscreens, and this use largely determines its global mining production. It is widely used in thin-films to form lubricated layers (during World War II it was widely used to coat bearings in high-performance aircraft). It is also used for making particularly low melting point alloys, and is a component in some lead-free solders.

Indium is not known to be used by any organism. In a similar way to aluminium salts, indium(III) ions can be toxic to the kidney when given by injection, but oral indium compounds do not have the chronic toxicity of salts of heavy metals, probably due to poor absorption in

basic conditions. Radioactive indium-111 (in very small amounts on a chemical basis) is used in nuclear medicine tests, as a radiotracer to follow the movement of labeled proteins and white blood cells in the body.

1.4 OBJECTIVE:

The objectives of the research are :

- To design a indium dopped silicon semiconductor.
- To prepare a sample for voltage drop study.
- To study the current dependent of the sample prepared.

Indium doped silicon has been grown from indium – rich solutions using a gradient – transport solution growth process. The growth temperatures were varied from 150^0c to 200^0c inside a micro-oven to determine the voltage drop of indium in silicon. The indium concentration obtainedin silicon. The growth process is described by one-dimensional diffusion .The solution –grown crystals were found to have a lower concentration of this shallower defect than melt grown crystals of the same indium concentration. The Oxygen and carbon concentrations are less because the sample is heated inside the microoven.

2.1literature review

2.1.1 NANOPARTICLES

Nanomaterials are applications with morphological features smaller than a one tenth of a micrometre in at least one dimension. Despite the fact that there is no consensus upon the minimum or maximum size of nanomaterials, with some authors restricting their size to as low as 1 to ~30 nm, a logical definition would situate the nanoscale between microscale (0.1 micrometre) and atomic/molecular scale (about 0.2 nanometers). An aspect of nanotechnology is the vastly increased ratio of surface area (second power of its linear dimensions) to volume (third power of its linear dimensions) present in many nanoscale materials which makes possible new quantum mechanical effects, for example the "quantum size effect" where the electronic properties of solids are altered with great reductions in particle size. This effect does not come into play by going from macro to micro dimensions. However, it becomes pronounced when the nanometer size range is reached. A certain number of physical properties also alter with the change from macroscopic systems. Novel mechanical properties of nanomaterials is a subject of nanomechanics research. Catalytic activities also reveal new behaviour in the interaction with biomaterials.

Nanotechnology can be thought of as extensions of traditional disciplines towards the explicit consideration of these properties. Additionally, traditional disciplines can be re-interpreted as specific applications of nanotechnology. This dynamic reciprocation of ideas and concepts contributes to the modern understanding of the field. Broadly speaking, nanotechnology is the synthesis and application of ideas from science and engineering towards the understanding

and production of novel materials and devices. These products generally make copious use of physical properties associated with small scales.

Electronic states of an atom are typically characterized by discrete energy levels that are often separated by electron volts. The spatial distribution of these states is highly localized. At the nanoscale, the dimension of energy states resides between these limits. Considering an electron of mass '*m*' confined within a one-dimension (1-D) box of size '*L*' and moving along x-axis inside the box, where potential energy $V(x) = 0$, the time-independent Schrodinger wave equation is given as [8]:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \tag{2.1}$$

Where E is the total energy of the particle, or

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \tag{2.2}$$

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \tag{2.3}$$

Where, $k = \sqrt{\frac{2mE}{\hbar^2}}$ (2.4)

For a particular value of the energy E, k is a constant.

The general solution of the above Eq. (2.3) is

$$\psi(x) = A\sin kx + B\cos kx \tag{2.5}$$

Where A and B are constant of integration. We have the boundary conditions: (a) at x =0, $\psi(x) = 0$ and (b) at $x = L$, $\psi(x) = 0$.

From the first condition, we get $B = 0$. Therefore, from Eq. (2.5) we have

$$\psi(x) = A \sin kx \tag{2.6}$$

Again, from the second boundary condition, we have

$$\psi(L) = A \sin kL = 0 \tag{2.7}$$

We cannot take A=0, because there will be no solution. Hence Eq. (2.7) is satisfied only when, $kL = n\pi$ (where n = 1, 2, 3….), or

$$kL = n\pi \tag{2.8}$$

We cannot take n = 0, because for n = 0, k = 0, E = 0 and hence $\psi(x) = 0$ everywhere in the box. This means that a particle with zero energy cannot present in the box. That is, a particle in a box, cannot have zero energy. Substituting the value of k from (2.8) in Eq. (2.4), we have

$$\sqrt{\frac{2mE}{\hbar^2}} = \frac{n\pi}{L} \tag{2.9}$$

From the above equation we get

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2} \tag{2.10}$$

This equation represents the eigen-values of the energy and is also called energy-levels of the particle. Since, $\hbar = \frac{h}{2\pi}$, we can have

$$E = \frac{n^2 h^2}{8mL^2} \tag{2.11}$$

The lowest energy level of this system is given by $E = (h^2 / 8\, m\, L^2)$, where 'h' is the Planck's constant and 'm' is the mass of the particle (electron). Since, $E \propto 1/\, L^2$, if size of the box (particle diameter) is reduced, then E increases, hence a drastic variation of its bulk properties. In the nanoscale phenomena, the energy level spacing of electronic states of atom increases with reduction in dimensionality of particle and is called Quantum Confinement (QC) [9], and is shown in Fig. 2.1. On the other word QC describes the increase in energy which occurs when the motion of a particle is restricted in one or more dimensions by a potential well. When the confining dimension is large compared to the wavelength of the particle, the particle behaves as if it were free. As the confining dimension decreased, the particle's energy increases.

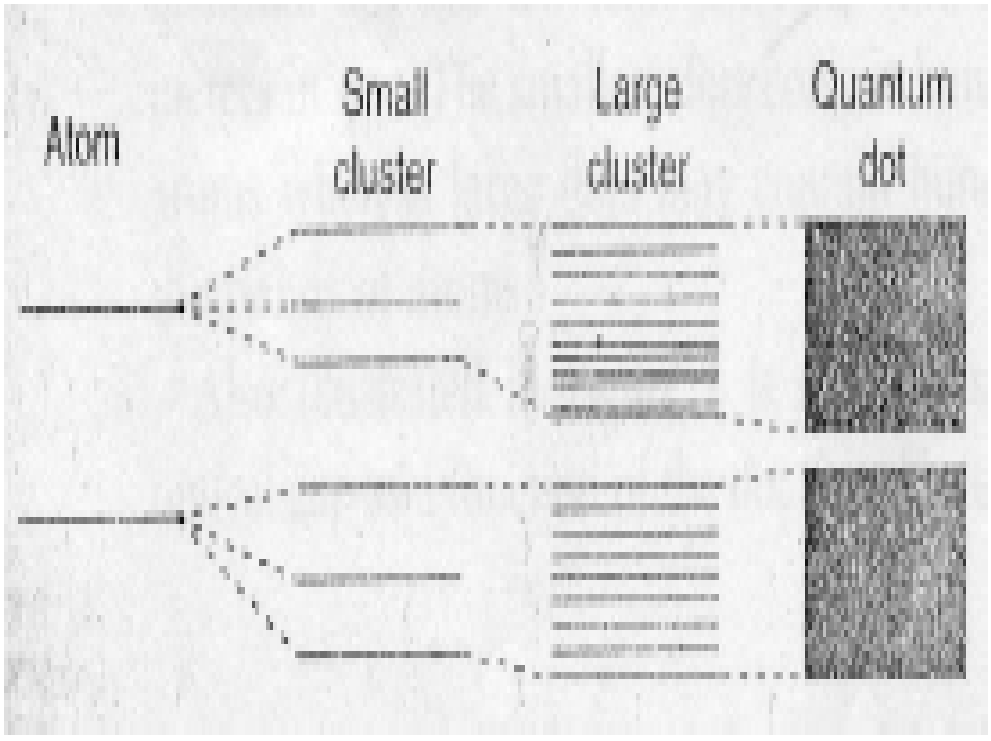


Fig. 2.1 Energy level diagram (atom, cluster and quantum dot)

The QC phenomena can be readily understood from the well known Heisenberg Uncertainty principle, which states that:

$$\Delta P.\Delta x = \hbar / 2 ,$$

$$\Delta P = \hbar / 2.\Delta x .$$

Where Δp- uncertainty in momentum, and Δx- uncertainty in position

A free electron confined within a 1-dimension box of size "*L*" (i.e. Δx)

$$\Rightarrow E \propto 1/(L)^2$$

Hence, if one tries to localize the position of an electron by reducing the box size (*L*), its energy must increases and diverge as the confining region vanishes.

Considering the energy of a free electron with momentum *P*, i.e.,

$$E = P^2 / 2m$$

Since the uncertainty in momentum cannot exceed the momentum itself *P*, i.e., $P > \Delta P$. So, the energy can be defined as $E < \hbar^2 / 8m L^2$. If one tries to localize the position of an electron by reducing the box size (*L*), its energy must increases and diverges as the confining region vanishes. QC can be experimentally observed in nanostructures quantum dots of Si and CdSe. Typically a quantum dot is a few nanometers to tens of nanometer size. The smallest dots contain hundreds of thousands of atoms. However, nanocrystalline materials are single-phase or multi-phase polycrystals, the crystal size of the order of 1-100 nm in at least 1-D. Depending on the QC and dimensions in which the length scale is nanometers, they can be classified [10] into:

(a) nanoparticles (0-D), (b) lamellar structure (1-D), (c) filamentary structure (2-D), and (d) bulk nanostructured (3-D) materials.

2.1.2 FERROELECTRICITY

Ferroelectricity is a spontaneous electric polarization of a material that can be reversed by the application of an external electric field. [11, 12]. The term is used in analogy to ferromagnetism, in which a material exhibits a permanent magnetic moment. Ferromagnetism was already known when ferroelectricity was discovered in 1920 in Rochelle salt by Valasek [13, 14]. Thus, the prefix *ferro*, meaning iron, was used to describe the property despite the fact that most ferroelectric materials do not have iron in their lattice.

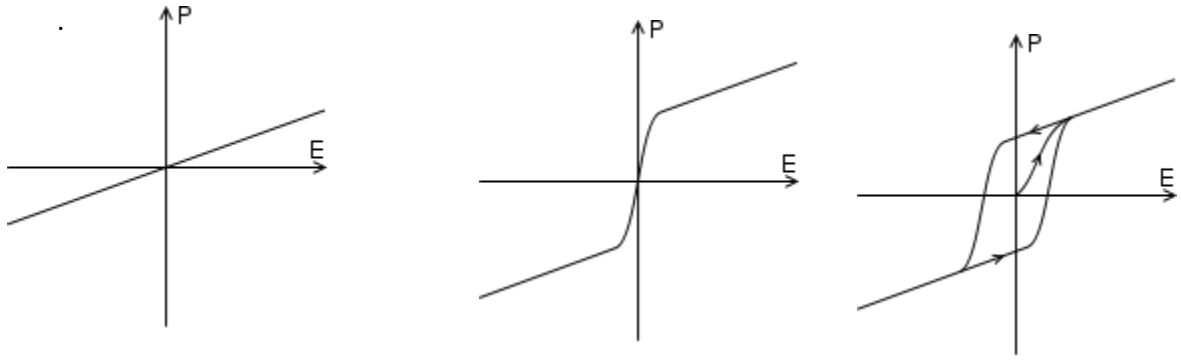


Fig. 2.2 Polarization: (a) Dielectric (b) Paraelectric (c) Ferroelectric

Most materials are polarized linearly with external electric field; nonlinearities are insignificant. This is called dielectric polarization, Fig. 2.2 (a). Some materials, known as paraelectric materials, demonstrate a more pronounced nonlinear polarization, Fig. 2.2 (b). The

electric permittivity, corresponding to the slope of the polarization curve, is thereby a function of the external electric field. In addition to being nonlinear, ferroelectric materials demonstrate a spontaneous polarization, Fig. 2.2 (c). Such materials are generally called pyroelectrics. The distinguishing feature of ferroelectrics is that the direction of the spontaneous polarization can be reversed by an applied electric field, yielding a hysteresis loop. Typically, materials demonstrate ferroelectricity only below a certain phase transition temperature, called the Curie temperature, T_c, and are paraelectric above this temperature.

2.1.3 PHYSICS OF FERROELECTRICITY

When the field F is reduced to zero a finite value of polarization called remanent polarisation P_r can be measured. In order to eliminate the remanent polarization P_r, an electric field of opposite direction must be applied. This is called the coercive force F_c. If the linear part of the hysteresis loop occurring at sufficiently large applied field strengths is extrapolated back to the polarization axis, one obtains the value of the spontaneous polarization P_S.

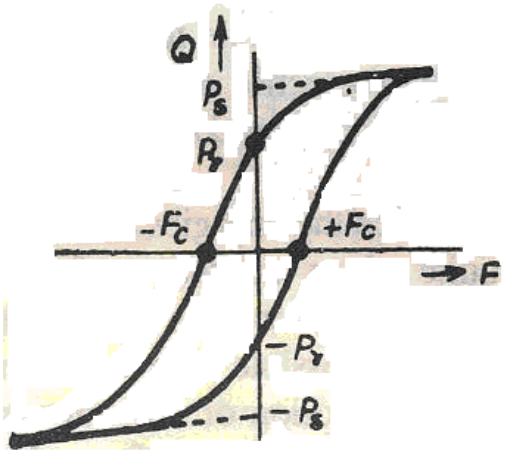


Fig. 2.3 Hysteresis Loop

The occurrence of hysteresis loop is understandable on the basis of the domain structure. In unpolarized materials a domain has equal chance of being polarized positively and negatively. If a field is applied, new positively polarized domains will grow at the expense of negatively polarized domains; the number of new domains increases at first slowly, then more rapidly, until finally all domains are lined up in the direction of the applied field. If the applied field is now reduced to zero many domains will remain aligned thus causing a permanent polarization P_r. An opposing electric field $-F_C$ has to be applied in opposite direction to remove this alignment. If the opposing field is large the material will gradually become polarized in opposite direction until saturation polarization sets in. If the field is now reduced to zero many domains remain aligned thus causing the remanent polarization $-P_r$; an opposing field $+F_C$ has to be applied to remove this alignment.

Energy is lost if the polarization is run through a complete cycle; the loss of energy per unit volume per cycle is $\oint E$ dP. This is important for a –c operation; if a sufficiently large signal of frequency *f* is applied, the power loss P_{hyst} of the sample is

$$P_{hyst} = \int V_S \oint F.dP$$

where *F* is the electric field and *V* is the volume of the sample.

A single crystal material is very suitable for the determination of the saturation polarization P_S. It is rather impossible to line up all the domains in the directions of the applied

field since in general the directions of preferred polarization of a crystallite do not coincide with the applied field; a polycrystalline material is not very suitable for a determination of P_S.

2.1.4 FERROELECTRICS

The internal electric dipoles of a ferroelectric material are coupled to the material lattice so anything that changes the lattice will change the strength of the dipoles (in other words, a change in the spontaneous polarization). The change in the spontaneous polarization results in a change in the surface charge. This can cause current flow in the case of a ferroelectric capacitor even without the presence of an external voltage across the capacitor. Two stimuli that will change the lattice dimensions of a material are force and temperature. The generation of a surface charge in response to the application of an external stress to a material is called piezoelectricity. A change in the spontaneous polarization of a material in response to a change in temperature is called pyroelectricity.

Ferroelectric phase transitions are often characterized as either displacive (such as $BaTiO_3$) and order-disorder (such as $NaNO_2$), though often phase transitions will have behavior that contains elements of both behaviors. In barium titanate, a typical ferroelectric of the displacive type, the transition can be understood in terms of a polarization catastrophe, in which, if an ion is displaced from equilibrium slightly, the force from the local electric fields due to the ions in the crystal increases faster than the elastic-restoring forces. This leads to an asymmetrical shift in the equilibrium ion positions and hence to a permanent dipole moment. The ionic displacement in barium titanate concerns the relative position of the titanium ion within the oxygen octahedral cage.

2.1.5 CHARACTERISTICS

Of the 32 possible crystal classes (i.e. point groups) 11 are Centro symmetric and thus cannot exhibit polar properties. The remaining 21 lack a center of symmetry and thus can posses one or more polar axes. Of these, 20 classes are piezoelectric (the one exception being cubic class 432). Piezoelectric crystals have the property that the application of mechanical stress induces polarization, and conversely, the application of an electric field produces mechanical deformation. Of the 20 piezoelectric classes, 10 have a unique polar axis and thus are spontaneously polarized, i.e. polarized in the absence of an electric field. Crystals belonging to polarized, i.e. polarized in the absence of an electric field. Crystals belonging to these 10 classes are called pyroelectric. The intrinsic polarization of pyroelectric crystals is often difficult to detect experimentally because of the neutralization of the charges on the crystal surfaces by free charges from the atmosphere and by conduction within the crystal. However, because the polarization is a function of temperature, it is often possible to observe the spontaneous moment in these crystals by changing the temperature, hence the name pyroelectrics. Ferroelectric crystals belong to the pyroelectric family, but they also exhibit the additional property that the direction of the spontaneous polarization can be reversed by the application of an electric field. Thus, we have the following simple definition for a ferroelectric crystal: **A ferroelectric crystals is a crystal that possess reversible spontaneous polarization as exhibited by a dielectric hysteresis loop.**

Although ferroelectric crystals are a widely varied group, they posses a number a general characteristics properties. Among these are the following:

- Which the crystal behaves as a normal dielectric. It should be noted, however, that in some crystals melting or chemical decomposition may occur before the Curie point is reached (e.g., the FE polymer PVDF).
- The hysteresis loop disappears at a certain temperature, the Curie point T_c, above at T_c a ferroelectric crystal transforms to a phase of higher symmetry. This higher temperature phase is usually nonpolar, or Para electric (PE).
- The polar crystal structure of a ferroelectric can be derived from the high-temperature PE structure by a slight distortion of the crystal lattice. This is the main reason behind the success of the phenomenological theory of Ferro electricity which assumes that the same free energy function is applicable for both the FE and PE phases.
- Ferroelectrics generally have a large static dielectric constant ε , or χ (= *P/E*, is the susceptibility), which rises to a peak value at T_c.
- Above T_c, ε of a ferroelectric (measured along the polar axis) usually obeys the Curie-Weiss law $\varepsilon = C/(T-T_0)$, where C and T_0 are the Curie-Weiss constant and Curie-Weiss temperature, respectively.

Finally, we should mention that there are substances which, on cooling, undergo a transition from a nonpolar to an anti polar state. In this state the crystal has a super lattice consisting a arrays of antiparallel dipoles. If, in a given crystal, the coupling energy between these arrays is comparable to that of the polar case, then the crystal is said to be anti ferroelectric (AFE). An anti ferroelectric crystal can usually be made ferroelectric by the application of a sufficiently large electric field.

2.1.6 THEORY OF FERROELECTRICITY

A shift of ionic positions as for Ti ion in $BaTiO_3$ is the key to Ferro electricity. Imagine a crystal just before it goes into ferroelectric phase. Suppose that an infinitesimal displacement of an ion from its equilibrium position occurs, then a local electric field is created on account of the dipole moment associated with the displacement. If the electric force overcomes the elastic restoring force a further displacement of the ion is expected. As displacement becomes appreciable anharmonic restoring forces set in and the ion finds itself in a new equilibrium position corresponding to the position which the ion occupies in the ferroelectric phase.

To explain the electric behavior of a specific ferroelectric crystal, a detailed knowledge of the particular arrangement of electric charges and forces in a given crystal structure is needed and then a specific model can be set up for the crystal under consideration [15]. Such model theories are available for Barium Titanate, Rochelle salt and potassium di hydrogen phosphate.

From the force balance we can write the following equation

$$A\,E_{loc} = Bx + Cx^3 + Dx^5$$

where E_{loc} is the local field acting on and x is the displacement of the ion under consideration and the constants A, B, C and D are proportionality constants. The terms involving x^3 and x^5 represent the anharmonic components of the restoring force. Since the dipole moment and in turn the polarisation P created by the displacement are directly proportional to x. Eq. (3.2) can be expressed in terms of P as

$$E_{loc} = aP + bP^3 + cP^5$$

The local field can also be written as

$$E_{loc} = E + f\,P$$

where E is the applied field and a general polarisation field $f P$ is used instead of the Lorentz field $P/3 \in_0$. Eqs. (3.4) with equation (3.3) gives

$$E = (a - f) P + bP^3 + cP^5$$

Therefore the internal energy of the system is equal to

$$U = \int EdP = \frac{(a-f)P^2}{2} + \frac{bP^4}{4} + \frac{cP^6}{6}$$

Two cases of particular interest in ferroelectric phase.

Case 1. (a - f) and c are positive while b is negative. In this case the spontaneous polarisation jumps discontinuously from zero to a finite value at the Curie temperature T_c. The zero value corresponds to the dielectric phase and the non-zero value to the ferroelectric phase. Since these two states exist simultaneously at T_c.

$$\frac{(a-f)P_s^2}{2} + \frac{bP_s^4}{4} + \frac{cP_s^6}{6} = U_p = U_0 = 0$$

where P_s is the spontaneous polarisation and the subscripts p and o refer to the polarised and unpolarized state respectively. Furthermore P_s exists in the absence of E, thus from we have

$$(a - f) + bP_s^2 + cP_s^4 = 0$$

Eqs. give the following results:

$$P_s^2(T_c) = -\frac{3b}{4c} = -\frac{4(a-f)}{b}$$

$$P_s^4(T_c) = \frac{3(a-f)}{c}$$

Case 2. $(f - a)$ and b are positive while c is negligible. It is obvious that with c = 0, the only solution of is

$$P_c^2(T_c) = 0 \text{ and } (f - a) = 0 \text{ at T = } T_c$$

Now let us look up the dielectric phase. Differentiating we get

$$\in - \in_0 = \frac{\partial P}{\partial E} = \frac{1}{a - f}$$

noting that the terms involving P_3 and P_5 are negligibly small compared to the linear term in P on account of the smallness of P in the dielectric phase.

For case (2) we can expand $(a - f)$ into a power series in terms of T-T_c. If only the first order term is kept, $\in - \in_0$ must be of the following form

$$\in - \in_0 = \frac{\beta}{T - T_c}$$

since $a - f = 0$ at T=T_c

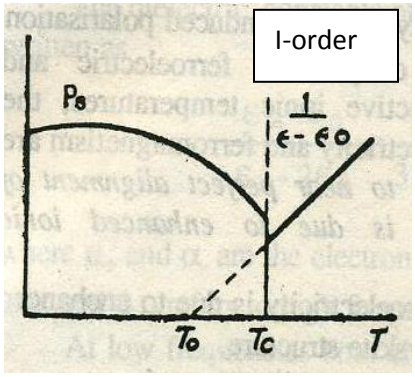
For case (1) $(a - f)$ is not zero at T=T_c. Therefore expansion at another *temperature* T_0 where $a - f$ is necessary. Thus for case (1) we have

$$\in - \in_0 = \frac{\beta}{T - T_0}$$

Behaviour of P_s and $\in$ as a function of temperature is illustrated in Fig. 2.4.

Case (1) and case (2) are known thermodynamically as first order and second order transitions respectively since case (1) involves a latent heat of transition while case II do not.

Barium Titanate shows the characteristics of a first order transition, potassium dihydrogen phosphate and Rochelle salt show the characteristics of a second order transition.



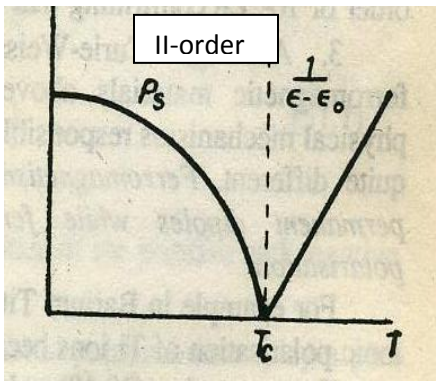


Fig. 2.4 The P_s and $\in$ as a function of temperature

Points of Interest

4. If ferroelectricity was due to an alignment of permanent dipoles the value of f should be different from *1/3* $\in_0$ even for crystals with cubic symmetry i.e. Lorentz's approach for internal field becomes inapplicable. Since Lorentz's approach is valid, the polarisation is included by a strain-inspired field.
5. If ferroelectricity was due to dipole alignment the value of β predicted is $\beta=3T_0\in_0$, while experimentally measured value of β is of the order of 10^5 $\in_0$ confirming that ferro electricity is due to induced polarization.
6. Although Curie-Weiss Law is obeyed in ferroelectric and ferromagnetic materials above their respective ionic temperatures, the physical mechanisms responsible for Ferro electricity and ferromagnetism are quite different. Ferromagnetism arises due to near perfect alignment of permanent dipoles while Ferro electricity is due to enhanced ionic polarization.

For example in Barium Titanate the Ferro electricity is due to enhanced ionic polarization of Ti ions because of Perovskite structure.

From Eq. (3.11) polarization catastrophe will occur when

$$\frac{\partial P}{\partial E} = \infty, i.e. (a - f) = 0$$

Since $a = \frac{1}{N\alpha}$ and $f = \frac{1}{3\in_0}$

Therefore polarisation catastrophe is expected when $\frac{N\alpha}{3\in_0} = 1$

The electronic contribution to the polarisability α can be estimated from the optical refractive index n of Ba TiO_3

$$\frac{n^2-1}{n^2+2}=\frac{N\alpha_e}{3\in_0}$$

For a value of n = 24, the value of $\frac{N\alpha_e}{3\in_0}$ is found to be 0.61. This leaves of value of 0.9 for ionic polarisation.

In Barium Titanate the Ti (ions) by their polarisation polarise the oxygen (type O_1) ions and these in turn act back on the Ti ions resulting in linear chains of dipoles. Since the oxygen (type O_1) ions in this linear chain do not possess cubic symmetry the field factor f is very much larger than $1/3\in_0$. It is thus great enhancement of the field at the Ti ion which causes the polarization of the Ti ion and makes the value of $fN\alpha_i(Ti)$ large enough for the polarization catastrophe.

Since the fundamental mechanics responsible for spontaneous polarization in many materials is not identifiable except for Barium Titanate which is most extensively investigated and best understood.

There are difficulties in formulating a unified theory of ferroelectricity. The ferroelectricity can be treated as a problem of lattice dynamics. It is a big step in establishing a unified theory. The basic idea behind the approach is relatively simple. In the ideal case of zero damping the dielectric constant of a crystal can be written in a general form [6].

$$\in(\omega)=\in_\infty+\sum\frac{b_i^2}{\omega_i^2-\omega^2}$$

Where $\in_\infty$ is high frequency (optical dielectric constant and the summation index i refers the ith optical mode of lattice vibration, ω_i^2 measures the strength of the restoring force and b_i^2 the strength of the coupling between the I vibrational mode to the electric field. According to Eq. (3.16) the static dielectric constant can be written as

$$\in_s = \in_\infty + \sum_i \frac{b_i^2}{\omega_i^2}$$

When the restoring force of one of the vibrational modes of lattice becomes very small at a given temperature, the static dielectric constant can become very large.

From the well known Szigeti relation and its other form defined in the book [14], one can define

$$\frac{M\omega_t^2}{r} = 1 - \frac{(\in_\infty + 2 \in_0) N(Ze)^2}{(3 \in_0)^2 r} = \eta(T - T_c)$$

By expanding the temperature dependence of certain atomic parameters into a Taylor's series at $T=T_c$ and where an effective ionic charge of Ze is assumed for sake of generality.

Simplifying applying advance theory of dielectrics [4], one can have

$$\in_s - \in_\infty = \frac{(\in_s + 2 \in_0)(\in_\infty + 2 \in_\infty)}{(3 \in_0)^2} \frac{N(Ze)^2}{r\eta(T - T_c)}$$

Eq. (3.19) is known as Curie-Weiss Law.

The condition for ferroelectricity ($(\in_s \to \infty)$ requires $T=T_c$ in the equation which in turn requires $\omega_1 \to 0$.

Therefore the theory of ferroelectricity is intimately connected with the theory of lattice Dynamics.

The condition for $\omega_t = 0$ from Ed. (3.18) can be written as

$$\frac{N(Ze)^2}{3\in_0 r} = 1 - \frac{\in_\infty - \in_0}{\in_\infty + 2\in_0} = 1 - \frac{N(\alpha_+ + \alpha_-)}{3\omega_0}$$

Realizing that $(Ze)^2/r$ is the ionic polarizability α_i at zero frequency, the equation gives

$$N(\alpha_i + \alpha_e)/3\in_0 = 1$$

Therefore the condition for polarizability catastrophe and the condition for $\omega_t = 0$ are the same.

2.1.7 ADVANCE THEORY

Based on Ginzburg–Landau theory, the free energy of a ferroelectric material, in the absence of an electric field and applied stress may be written as a Taylor expansion in terms of the order parameter, *P* [7]. If a sixth order expansion is used (i.e. 8th order and higher terms truncated), the free energy is given by:

$$\begin{aligned}\Delta G = \; & \tfrac{1}{2}\alpha_0 (T - T_0)\left(P_x^2 + P_y^2 + P_z^2\right) + \tfrac{1}{4}\alpha_{11}\left(P_x^4 + P_y^4 + P_z^4\right) \\ & + \tfrac{1}{2}\alpha_{12}\left(P_x^2 P_y^2 + P_y^2 P_z^2 + P_z^2 P_x^2\right) \\ & + \tfrac{1}{6}\alpha_{111}\left(P_x^6 + P_y^6 + P_z^6\right) \\ & + \tfrac{1}{2}\alpha_{112}\left[P_x^4\left(P_y^2 + P_z^2\right) + P_y^4\left(P_x^2 + P_z^2\right) + P_z^4\left(P_x^2 + P_y^2\right)\right] \\ & + \tfrac{1}{2}\alpha_{123} P_x^2 P_y^2 P_z^2\end{aligned}$$

where P_x, P_y, and Pz are the components of the polarization vector in the *x, y,* and *z* directions respectively, and the coefficients, α_i, α_{ij}, α_{ijk} must be consistent with the crystal symmetry. To investigate domain formation and other phenomena in ferroelectrics, these equations are often used in the context of a phase field model. Typically, this involves adding a gradient term, an electrostatic term and an elastic term to the free energy. The equations are then discretized onto a grid using the finite difference method and solved subject to the constraints of Gauss's law and Linear elasticity.

In all known ferroelectrics, $\alpha_0 > 0$ and $\alpha_{111} > 0$. These coefficients may be obtained experimentally or from ab-initio simulations. For ferroelectrics with a first order phase transition, $\alpha_{11} < 0$ and $\alpha_{11} > 0$ for a second order phase transition.

The spontaneous polarization, P_s of a ferroelectric for a cubic to tetragonal phase transition may be obtained by considering the 1D expression of the free energy which is:

$$\Delta G = \frac{1}{2}\alpha_0 \left(T - T_0\right) P_x^2 + \frac{1}{4}\alpha_{11} P_x^4 + \frac{1}{6}\alpha_{111} P_x^6$$

This free energy has the shape of a double well potential with two free energy minima at $P = \pm P_s$, where P_s is the spontaneous polarization. At these two minima, the derivative of the free energy is zero, i.e.:

$$\frac{\partial \Delta G}{\partial P_x} = \alpha_0 \left(T - T_0\right) P_x + \alpha_{11} P_x^3 + \alpha_{111} P_x^5 = 0$$

$$P_x \left[\alpha_0 \left(T - T_0\right) + \alpha_{11} P_x^2 + \alpha_{111} P_x^4\right] = 0$$

Since $P_x = 0$ corresponds to a free energy maxima in the ferroelectric phase, the spontaneous polarization, P_s, is obtained from the solution of the equation:

$$\alpha_0 \left(T - T_0\right) + \alpha_{11} P_x^2 + \alpha_{111} P_x^4 = 0$$

which is:

$$P_s^2 = \frac{1}{2\alpha_{111}} \left[-\alpha_{11} \pm \sqrt{\alpha_{11}^2 - 4\alpha_0 \alpha_{111} \left(T - T_0\right)}\right]$$

and elimination of solutions yielding a negative square root (for either the first or second order phase transitions) gives:

$$P_s = \sqrt{\frac{1}{2\alpha_{111}} \left[-\alpha_{11} + \sqrt{\alpha_{11}^2 - 4\alpha_0 \alpha_{111} \left(T - T_0\right)}\right]}$$

If $\alpha_{111} = 0$, using the same approach as above, the spontaneous polarization may be obtained as:

$$P_s = \sqrt{-\frac{\alpha_0 \left(T - T_0\right)}{\alpha_{11}}}$$

The hysteresis loop (P_x versus E_x) may be obtained from the free energy expansion by adding an additional electrostatic term, $E_x P_x$, as follows:

$$\Delta G = \frac{1}{2}\alpha_0 (T - T_0) P_x^2 + \frac{1}{4}\alpha_{11} P_x^4 + \frac{1}{6}\alpha_{111} P_x^6 - E_x P_x$$

$$\frac{\partial \Delta G}{\partial P_x} = \alpha_0 (T - T_0) P_x + \alpha_{11} P_x^3 + \alpha_{111} P_x^5 - E_x = 0 \qquad (3.30)$$

$$E_x = \alpha_0 (T - T_0) P_x + \alpha_{11} P_x^3 + \alpha_{111} P_x^5$$

Plotting E_x as a function of P_x and reflecting the graph about the 45 degree line gives an 'S' shaped curve. The centre part of the 'S' corresponds to a free energy local maximum (since $\frac{\partial^2 \Delta G}{\partial P_x^2} < 0$). Elimination of this region, and connection of the top and bottom portions of the 'S' curve by vertical lines at the discontinuities gives the hysteresis loop.

2.1.8 APPLICATIONS

The nonlinear nature of ferroelectric materials can be used to make capacitors with tunable capacitance. Typically, a ferroelectric capacitor simply consists of a pair of electrodes sandwiching a layer of ferroelectric material. The permittivity of ferroelectrics is not only tunable but commonly also very high in absolute value, especially when close to the phase transition temperature. This fact makes ferroelectric capacitors small in size compared to dielectric (non-tunable) capacitors of similar capacitance.

The spontaneous polarization of ferroelectric materials implies a hysteresis effect which can be used as a memory function. Indeed, ferroelectric capacitors are used to make ferroelectric RAM [18] for computers and RFID cards. These applications are usually based on thin films of ferroelectric materials as this allows the high coercive field required to switch the polarization to

be achieved with a moderate voltage, though a side effect of this is that a great deal of attention needs to be paid to the interfaces, electrodes and sample quality for devices to work reliably [19]. All ferroelectrics are required by symmetry considerations to be also piezoelectric and pyroelectric. The combined properties of memory, piezoelectricity, and pyroelectricity make ferroelectric capacitors very useful, e.g. for sensor applications. Ferroelectric capacitors are used in medical ultrasound machines (the capacitors generate and then listen for the ultrasound ping used to image the internal organs of a body), high quality infrared cameras (the infrared image is projected onto a two dimensional array of ferroelectric capacitors capable of detecting temperature differences as small as millionths of a degree Celsius), fire sensors, sonar, vibration sensors, and even fuel injectors on diesel engines. As well, the electro-optic modulators that form the backbone of the Internet are made with ferroelectric materials.

One new idea of recent interest is the *ferroelectric tunnel junction* (*FTJ*) in which a contact made up by nanometer-thick ferroelectric film placed between metal electrodes. The thickness of the ferroelectric layer is thin enough to allow tunneling of electrons. The piezoelectric and interface effects as well as the depolarization field may lead to a giant electroresistance (GER) switching effect.

Another hot topic is multiferroics, where researchers are looking for ways to couple magnetic and ferroelectric ordering within a material or heterostructure; there are several recent reviews on this topic [20-23]. Cross-section

3.1 EXPERIMENTAL

Human endeavor towards continuous improvement in the quality of life has resulted in a host of advance materials and new technologies. There is a wide variety of the behavior of materials, but a great chasm exists between the experimental results and the ability of the theoretician to predict these results. Of course, the serious experimentalist has the upper hand in this game, since he reports the newer phenomena. Accuracy of the experimental results depends on seriousness of experimenter and sophistication of instruments.

Silicon

Silicon, a tetravalent metalloid, is a chemical element with the symbol **Si** and atomic number 14. Silicon is the eighth most common element in the universe by mass, but very rarely occurs as the pure free element in nature. It is most widely distributed in dusts, sands, planetoids, and planets as various forms of silicon dioxide (silica) or silicates. Most silicon is used commercially without being separated, and indeed often with little processing of compounds from nature. Although most free silicon is used in the steel refining, aluminum-casting, and fine chemical industries (often to make fumed silica), the relatively small portion of very highly purified silicon that is used in semiconductor electronics (< 10%) is perhaps even more critical.

Name, symbol,number	silicon, Si, 14
Element category	metalloid
Group, period,block	14, 3, p
Standard atomic weight	28.085(1)
Electron configuration	[Ne] $3s^2$ $3p^2$
Phase	solid
Density(near r.t.)	2.3290 $g \cdot cm^{-3}$
Liquid density atm.p.	2.57 $g \cdot cm^{-3}$
Melting point	1687 K, 1414 °C, 2577 °F
Boiling point	3538 K, 3265 °C, 5909 °F
Heat of fusion	50.21 $kJ \cdot mol^{-1}$
Heat of vaporization	359 $kJ \cdot mol^{-1}$
Molar heat capacity	19.789 $J \cdot mol^{-1} \cdot K^{-1}$

Indium

Indium is a chemical element with symbol In and atomic number 49. This rare, very soft, malleable and easily fusible post transition metal is chemically similar to galliumand thallium, and shows intermediate properties between these two. Indium's current primary application is to form transparent electrodes from indium tin oxide (ITO) in liquid crystal displays and touchscreens, and this use largely determines its global mining production. It is widely used in thin-films to form lubricated layers. Indium is not known to be used by any

organism. In a similar way to aluminium salts, indium(III) ions can be toxic to the kidney when given by injection, but oral indium compounds do not have the chronic toxicity of salts of heavy metals, probably due to poor absorption in basic conditions. Radioactive indium-111 (in very small amounts on a chemical basis) is used in nuclear medicine tests, as a radiotracer to follow the movement of labeled proteins and white blood cells in the body.

Name, symbol,number	indium, In, 49
Pronunciation	/□ɪ ndiəm/ ***ɪn-dee-əm***
Element category	post-transition metal
Group, period,block	13, 5, p
Standard atomic weight	114.818
Electron configuration	[Kr] $4d^{10}\ 5s^2\ 5p^1$
Phase	solid
Density(near r.t.)	7.31 $g{\cdot}cm^{-3}$
Liquid density atm.p.	7.02 $g{\cdot}cm^{-3}$
Melting point	429.7485 K, 156.5985 °C, 313.8773 °F
Boiling point	2345 K, 2072 °C, 3762 °F
Heat of fusion	3.281 $kJ{\cdot}mol^{-1}$
Heat of vaporization	231.8 $kJ{\cdot}mol^{-1}$
Molar heat capacity	26.74 $J{\cdot}mol^{-1}{\cdot}K^{-1}$

Doping semiconductor

In semiconductor production, **doping** intentionally introduces impurities into an extremely pure (also referred to as *intrinsic*) semiconductor for the purpose of modulating its electrical properties. The impurities are dependent upon the type of semiconductor. Lightly and moderately doped semiconductors are referred to as *extrinsic*. A semiconductor doped to such high levels that it acts more like a conductor than a semiconductor is referred to as *degenerate*.

Carrier concentration

The concentration of dopant introduced to an intrinsic semiconductor determines its concentration and indirectly affects many of its electrical properties. The most important factor that doping directly affects is the material's carrier concentration. In an intrinsic semiconductor under thermal equilibrium, the concentration of electrons and holes is equivalent. That is,

$$n = p = n_i.$$

If we have a non-intrinsic semiconductor in thermal equilibrium the relation becomes:

$$n_0 \cdot p_0 = n_i^2$$

Where n_0 is the concentration of conducting electrons, p_0 is the electron hole concentration, and n_i is the material's intrinsic carrier concentration. Intrinsic carrier concentration varies between materials and is dependent on temperature. Silicon's n_i, for example, is roughly 1.08×10^{10} cm^{-3} at 300 kelvin (room temperature).[4]

In general, an increase in doping concentration affords an increase in conductivity due to the higher concentration of carriers available for conduction. Degenerate (very highly doped) semiconductors have conductivity levels comparable to metals and are often used in modern integrated circuits as a replacement for metal. Often superscript plus and minus symbols are used to denote relative doping concentration in semiconductors. For example, n^+ denotes an n-type semiconductor with a high, often degenerate, doping concentration. Similarly, p^- would indicate a very lightly doped p-type material. Even degenerate levels of doping imply low concentrations of impurities with respect to the base semiconductor. In crystalline intrinsic silicon, there are approximately 5×10^{22} atoms/cm^3. Doping concentration for silicon semiconductors may range anywhere from 10^{13} cm^{-3} to 10^{18} cm^{-3}. Doping concentration above about 10^{18} cm^{-3} is considered

degenerate at room temperature. Degenerately doped silicon contains a proportion of impurity to silicon on the order of parts per thousand. This proportion may be reduced to parts per billion in very lightly doped silicon. Typical concentration values fall somewhere in this range and are tailored to produce the desired properties in the device that the semiconductor is intended for.

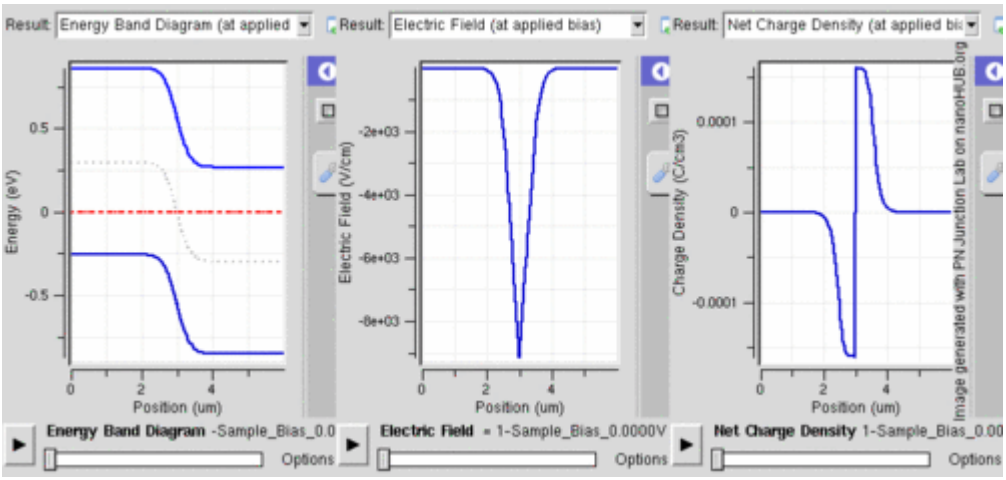


Fig.3.1

Band diagram of PN junction operation in forward bias mode showing reducing depletion width. Both p and n junctions are doped at a $1\times10^{15}/cm^3$ doping level, leading to built-in potential of ~0.59 V. Reducing depletion width can be inferred from the shrinking charge profile, as fewer dopants are exposed with increasing forward bias [1].

Doping a semiconductor crystal introduces allowed energy states within the band gap but very close to the energy band that corresponds to the dopant type. In other words, donor impurities create states near the conduction band while acceptors create states near the valence band. The gap between these energy states and the nearest energy band is usually referred to as dopant-site bonding energy or $E_B$and is relatively small. For example, the E_B for boron in silicon bulk is 0.045 eV, compared with silicon's band gap of about 1.12 eV. Because E_B is so small, it takes little energy to ionize.

Apparatus used in the experiment:

1. Micro-oven: capacity 20ltrs, power 4048GW

Fig.3.2: micro oven

2. Wheat powder

3. Sample: Silicon(single crystal)(111) plane

Indium

4. Variable resister:

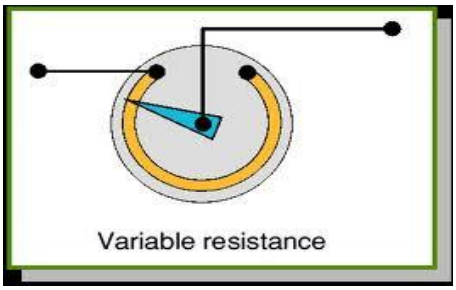


Fig.3.3: variable Resister

A variable resistor is usually a long coiled wire with hundreds of turns. It is also known by the name of rheostat. Actually, all wires have resistance. You can make a variable resistor out of any material. What happens is that there is a sliding contact along the length of the coil. One end

provides the least resistance while the other end provides the maximum resistance. This is so because in the second case, electricity has to go through the entire wire coil and hence there is greater resistance to it. You can get the desired level of resistance from the resistor by sliding the contacts.

5. Battery. 9 volt

6. Multimeter: As the name suggests, multimeters are those measuring instruments which can be used to calculate multiple circuit characteristics. Making them digital gives highly precise outputs as unlike their analog counterparts, there is no needle whose pointer is to be figured out. How are the digital meters more advanced than their predecessor? What internal circuitry is there to power such quick and rapid calculations? Just simply hook it to the circuit and take readings on the fly? Multimeter does that for us. So let us explore the Nitty Gritties of the Multimeter that make it a jack of many (if not all) trades of electrical measurements.

Fig3.4: multimeter

Working Principle:

We have tested 4 silicon samples. First we studied the properties of normal silicon sample. Secondly a silicon sample is heated for 3 minutes inside the micro-oven. Third silicon sample is heated with Indium doping for 3 minutes. Fourth sample is heated for 5 minutes with Indium doped.

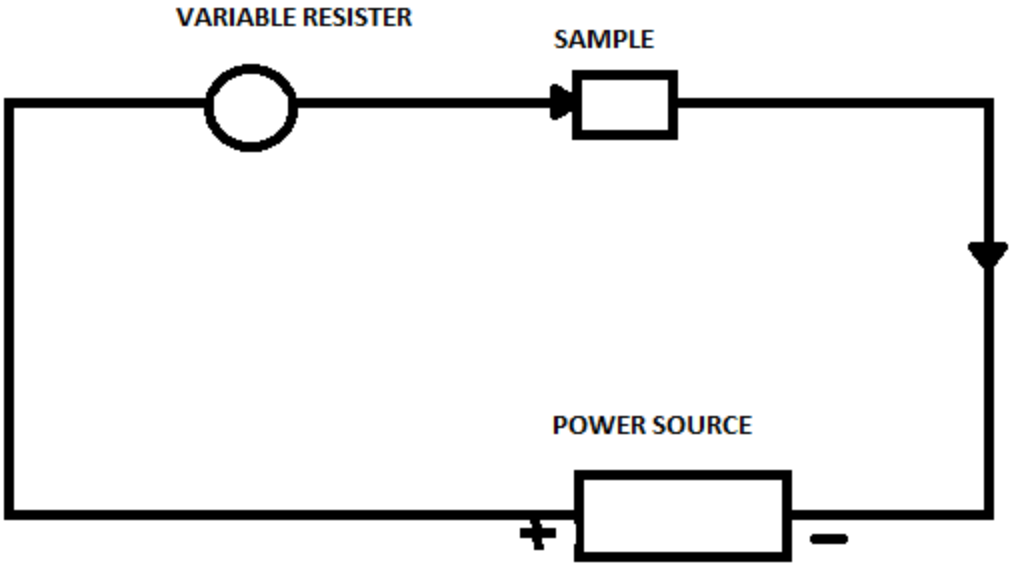


Fig.3.5: circuit diagram of to measure the V-I characteristic

As shown in the figure the current is taken from the power source, then it goes to the variable register to get required amount of current. Then using different samples are used. After that we calculate the voltage drop by using multmeter.

Indium doped silicon has been grown from indium – rich solutions using a gradient – transport solution growth process. The growth temperatures were varied from 150^0c to 200^0c inside a micro-oven to determine the voltage drop of indium in silicon. The indium concentration obtainedin silicon. The growth process is described by one-dimensional diffusion .The solution – grown crystals were found to have a lower concentration of this shallower defect than melt grown crystals of the same indium concentration. The Oxygen and carbon concentrations are less because the sample is heated inside the microoven. Cross-section

RESULTS AND DISCUSSION

V-I characteristics:

Indium doped silicon has been grown from indium – rich solutions using a gradient – transport solution growth process. The growth temperatures were varied from 150^0c to 200^0c inside a micro-oven to determine the voltage drop of indium in silicon. The indium concentration obtained in silicon. The growth process is described by one-dimensional diffusion .The solution –grown crystals were found to have a lower concentration of this shallower defect than melt grown crystals of the same indium concentration. The Oxygen and carbon concentrations are less because the sample is heated inside the microoven. Cross-section

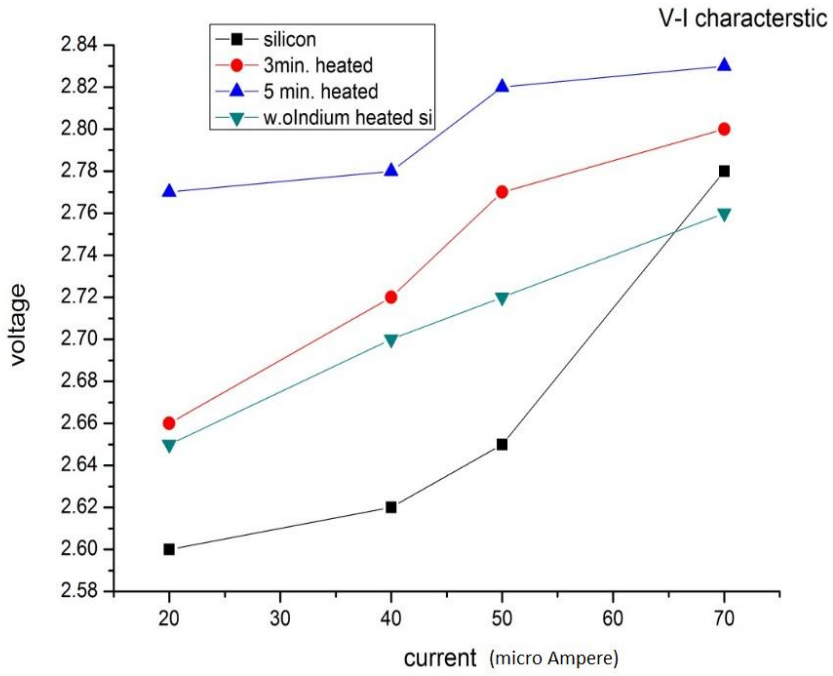


Fig.4.1: V-I Characteristic

From the graph it is concluded that:

- The SQUARE line shows the voltage drop of silicon in normal condition.
- The ARROW line shows the variation of voltage drop when heated without doping
- The CIRCLED line shows voltage drop with Indium doped when heated for 3 minutes.
- The TRIANGLE line shows the voltage drop with indium doped when heated for 5 minutes.

From the above figure it is found that there is a sharp voltage drop of Silicon without In doping. But for the sample after doping with In and heated in micro-oven the voltage drop is different, i.e. there is sharp drop of voltage between 40-50 µA current range. Which is more essential for semiconductor devices.

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XRD Analysis

From the experiment it is found that after indium doping there is a compound Peak formed ($BaMnSiO_4$,$Cs_2Si_2O_5$).this is the difference found after Indium doping on silicon inside the micro oven.

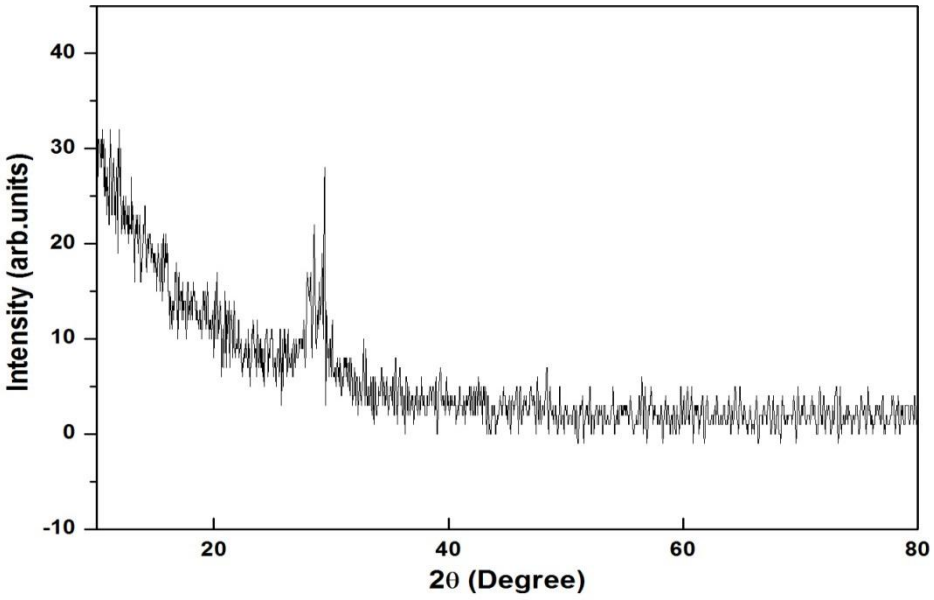

Fig 4.2 (a) Si single crystal

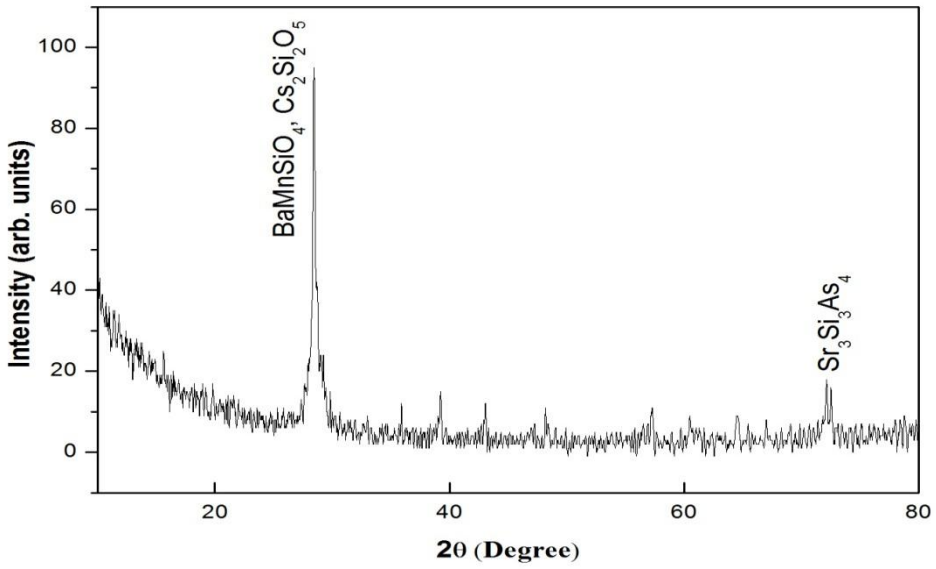

Figure 4.2(b) Si doped with Indium

The XRD analysis of the samples are shown in figure4.2 and 4.2a shows the silicon peak.Where as the samples after doping with indium figure4.2(b)exhibits the formation of $SrSiSs_4$,$BaMnSiO_4$ and $Cs_2Si_2O_6$phases.These phases might be responsible for change in V-I characterstic than that of silicon crystal.

SEM Analysis

Precipitation in grain observed in SEM view. That may be responsible for Voltage drop in the Indium doped Silicon sample.

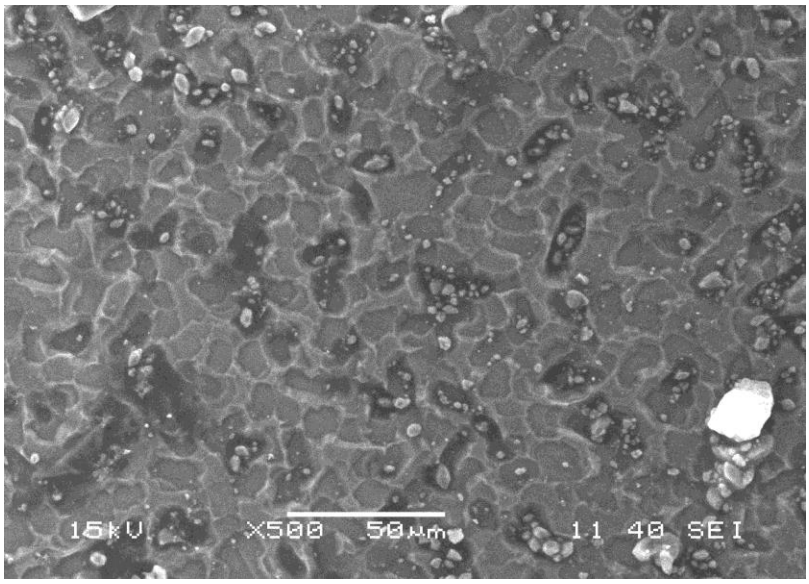

Figure4.3: Microstructure of a silicon single crystal

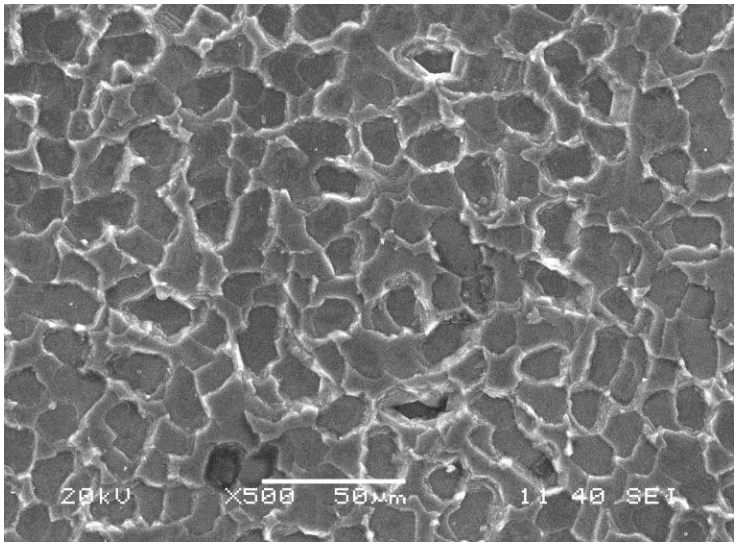

Fig.4.4(a)

Microstructure of a silicon single crystal after 3 min. heating.

From the above structure it is found that there are some precipited single crystal without treatment .after heating 3 min inside the micro-oven no precipited is found that is homogenize structure is obtained.

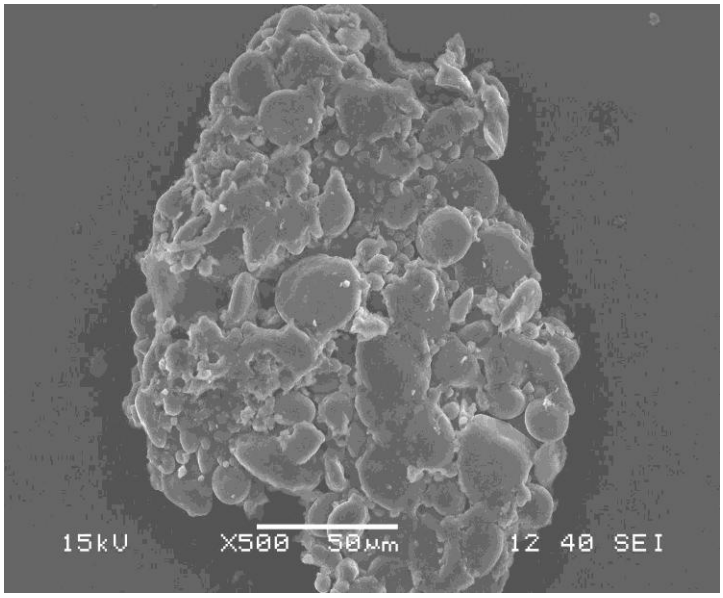

Fig 4.4(b)

Figure shows that after 3minutes heated inside the micro-oven, white spot shows Indium and the black spot is the silicon. There is no crystal structure comes for silicon.

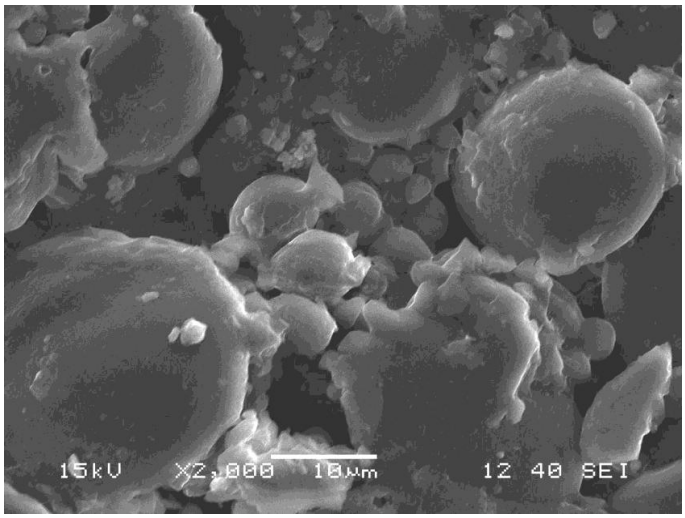

Fig.4.5:

Fig 4.5 shows the micro structure after doping globular precipitate seen may be the phase form as observed in XRD.

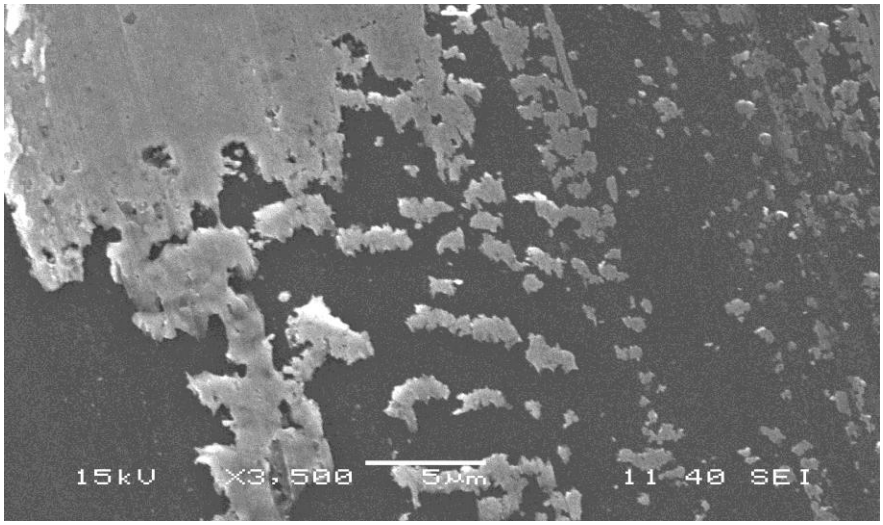

Fig 4.6

Fig 4.6 shows the micro structure of sample after heating 5 minute inside the micro oven it typical magnified view of the surface. It shown in figure 4.7. It can be visualized the its shape and size become elongated may be due to growth and coalescences of the particle.

The variation in the PI characteristics in Indium 2 and un dope sample for different time is due to the observed structural changes.

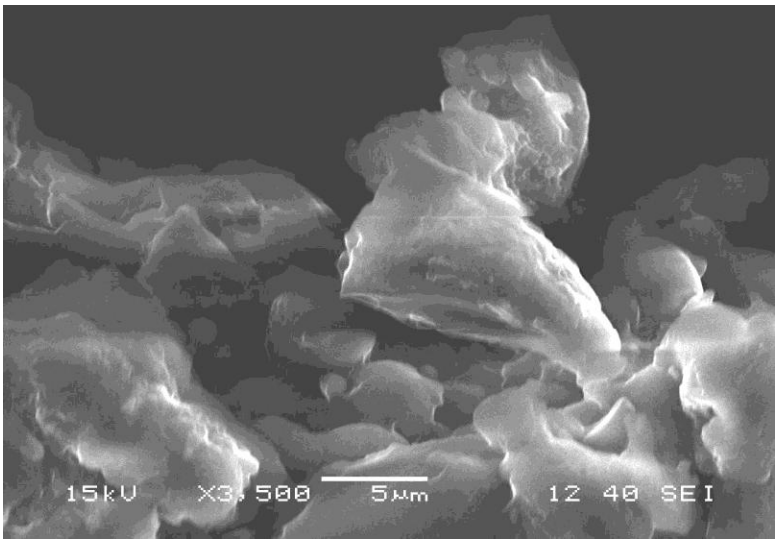

Fig.4.7

Figure 4.7 shows after 3 minutes heated inside the micro-oven, and magnifying 3500,It is found that the white spots are Indium and the black spots are Silicon.

CONCLUSION

From the investigation it can be concluded that:

1. There is a maximum voltage drop in between 40 – 50 micro-ampere in indium doped silicon metal which is heated for 3-5 minutes.

2. In XRD analysis we have found that there is a peak difference comes when an indium doped silicon metal is heated.

3. Precipitation in grain observed in SEM view. That may be responsible for Voltage drop in the Indium doped Silicon sample.

FUTURE WORK

5. Different concentration of indium doping may carried out to study V-I characteristics.
6. 2. Different heating time may be done.
7. Different dose of the indium doping can be made.
8. Effect of temperature in solubility may study.

REFERENCE

[1] Resistance www.wikipedia.com

[2] W. Cochran, *Phy. Rev. Lett.* 3 (1959) 412.

[3] D. Henning, A. Schnell, G. Simon, *J. Am. Ceram. Soc*., 65 (1982) 539.

[4] Z. Yu, R. Guo, A. S. Bhalla, *J.Appl. Phys,* 88 (2000) 410.

[5] S. Lee, T. Son, J. Yun, H. Kwon, G. L. Messing, B. Jun, *Mat. Lett.* 28 (2004) 2932.

[6] A. Testinon, M. T. Buscaglia, M. Viviani, V. Buscaglia, P. Nanni, *J. Am. Ceram. Soc*., 87 (2008) 79.

[7] W. Xiao, X. Gang, R. Zhaohui, S. Ge, H. Georong, *J. Am. Ceram. Soc*., 91 (2008) 3774.

[8] S. P. Singh, M. K. Bagde, Quantum Mechanics (S. Cand & Company Ltd., New Delhi , 1992), p.131.

[9] J. R. Chelikowsky, Encyclopedia of Condensed Matter Physics in: F. Bassani, G. L. Liedl,P. Wyder (Eds.), (Oxford, 2005), p. 51.

[10] C. Suryanarayana, C.C. Koch in: C. Suryanarayana, (Ed.), Non-Equilibrium Processing Of Materials (Pergamon, New York, 1999), p. 313–344

[11] W. Känzig, *Ferroelectrics and Antiferroelectrics* in F. Seitz, T. P. Das, D. Turnbull, E. L Hahn, *Solid State Physics*. **4**. (Academic Press, 1957) p.5.

[12] M. Lines, A. Glass, *Principles and applications of ferroelectrics and related materials* (Clarendon Press, Oxford, 1979).

[13] J. Valasek, *Phys. Rev.* **17** (1921) 475.

[14] B. S. Saxena, R. C. Gupta, P. N. Saxena, *Fundamentals of Solid State Physics* (Pragati Prakashan, Meerut, 1995) p.626.

[15] M. Born, K. Huang, *Dynamic Theory of Crystal Lattice* (Clarenden Press, Oxford, 1954).

[16] Ferroelectricity, *www.wikipedia.com*

[17] J. F. Scott, *Ferroelectric Memories* (Springer, 2000).

[18] M. Dawber, K.M. Rabe, J.F. Scott, *Rev. Mod. Phys.* **77** (2005) 1083.

[19] R. Ramesh, N.A Spaldin, *Nature Mat.* **6** (2007) 21.

[20] W. Eerenstein, N.D. Mathur, J.F. Scott, *Nature* **442** (2006) 759.

[21] N.A. Spaldin, M. Fiebig, *Science* **309** (2005) 5391.

[22] M. Fiebig *J. Phys. D: Appl. Phys.* **38** (2005) R123.

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